CHEMOURS DELISLE PLANT

2017 HWDIR EXEMPTION PETITION REISSUANCE APPLICATION

SECTION 6.0 WASTE COMPATIBILITY

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6.0 WASTE COMPATIBILITY

This section contains a description of the waste stream and an evaluation of waste compatibility testing from laboratory test results, as well as 37 years of well operations. Compatibility testing predicts whether individual waste streams or a combination of waste streams will affect either the confining or injection formations or the mechanical integrity of the waste well. Three major areas of compatibility were evaluated and reviewed: waste to waste, waste to formation, and waste to materials of construction.

Section 6.1 describes the waste stream characteristics, sample collection, and sample analysis. Section 6.2 focuses on the compatibility of the waste stream(s) with the geologic formation and formation fluid. Section 6.3 describes the compatibility of the waste stream with the materials of well construction, such as casing, tubing, packers, screen, liner, and cement.

6.1 Waste Stream Description

The waste stream at the DeLisle Plant is an aqueous solution of iron chloride, other metal chlorides, and hydrochloric acid. The hydrochloric acid is generated from air emission abatement control facilities. The exact make-up of the iron and miscellaneous chloride constituents of the waste stream varies, depending on the grade of ilmenite ore used and the exact mineral mix of its composition.

6.1.1 Waste Stream Analysis

Tables 6-1 through 6-3 provide a representative characterization of the waste stream, refer to Appendix 6-3 for a full analytical report.

Only those parameters required to be monitored by the previous MDEQ UIC Permit No. MSI-1001 have historical data ranges. These ranges are given in Table 6-4 to reflect historical values for the last three calendar years through the end of March 2016.

6.1.2 Waste Stream Sampling Protocol

6.1.2.1 Current Waste Stream Sampling

Part I Section C.1 of MDEQ UIC Permit No. MSI-1001 prescribes the analytical methods to be used for routine monitoring of the composition of the injected waste stream as 40 CFR 136, and 40 CFR 261 Appendix A.

MDEQ UIC Permit No. MSI-1001 requires collection of monthly flow-proportional composite samples to be analyzed for the parameters listed in Part I Section C.2. The proposed version of the permit (included in Appendix 1-1 of this application) requires monthly monitoring of the following metals (composite sample) to clearly indicate the presence of iron chloride waste from the DeLisle Plant:

- Temperature
- Flow Rate
- Volume
- Total Acidity
- Specific Gravity
- Total Iron
- Total Chromium
- Total Vanadium
- Total Lean
- Total Manganese
- Volatile Organic Compounds

6.1.2.3 Sampling Techniques

Samples of the injected waste fluid are collected by an automated deepwell sampler located in the suction of each well's transfer pump. The samplers take samples in proportion to flow volumes on a continuous basis of the iron chloride being injected down each well. The continuous samples collected by the four automated flow-proportional samplers are collected in a single five-gallon plastic bottle to form a single weekly sample. The weekly sample is taken to the DeLisle Plant's Control Lab where it is mixed with the other 3-4 weekly samples to form a single monthly composite sample. A representative aliquot of the monthly composite is sent to a third-party EPA-certified laboratory for analysis by the analytical methods prescribed by permit MSI1001 issued by the Mississippi Department of Environmental Quality. The automatic deepwell samplers are inspected a minimum of twice per shift to ensure that:

1) The sampler is in Auto mode, unless otherwise stated,
2) A sample is being taken,
3) The sample container top is secured, and
4) The container is checked for leaks.

If the automatic deepwell sampler is not operating satisfactorily, a daily 500-milliliter composite sample is collected in a labeled container from the transfer pump suction drain on an hourly basis. The hourly samples are combined for the daily composite sample in proportion to flow rates at the end of 24 hours to make one 500 milliliter sample. The daily samples are then combined weekly in proportion to flow rates to produce a 500 milliliter composite sample. The weekly samples are combined to produce a monthly composite sample for the monthly analysis that is reported to the state of Mississippi.

For manual sampling, the site uses a procedure to train personnel responsible for taking the samples described above. Every employee that is new to the job is trained, and experienced employees are trained every three years and have to demonstrate proficiency in the skills required by the procedure. Composite samples are dated and labeled with initials.

6.1.2.4 Sampling Analysis

Composite samples are delivered to an accredited commercial laboratory for analysis. Appendix 6-1 is an analytical report for a typical monthly iron chloride sample. Appendix 6-2 is an analytical report for a typical quarterly volatile organic compounds sample using Method 8260 as described in EPA publication SW-846. The analytical report for the sample whose results are summarized in the table in section 6.1.1 is enclosed as Appendix 6-3.

6.1.3 Quality Assurance/Quality Control

The analytical reports in Appendices 6-1, 6-2 and 6-3 contain a quality control section that describes the procedures used by the laboratory to ensure the accuracy of reported values. The laboratory conducts internal tests to determine its own specific method reporting limits (MRL) for each parameter measured by each applicable analytical method. The laboratory performing the analyses shown in Appendices 6-1, 6-2 and 6-3 is accredited by the National Environmental Lab Accreditation program with accreditation number TNI01397.

Note the following samples are generally analyzed: 1) a blank, 2) a known low concentration sample, 3) a duplicate known low concentration sample, and 4) a duplicate of the sample being analyzed.

A chain of custody is filled out before the samples are turned over to the custody of analytical laboratory personnel. Appendices 6-1, 6-2 and 6-3 contain copies of the sample chain of custody forms.

6.2 Hydrogeologic Compatibility

Hydrogeologic compatibility tests identify anticipated reaction products and demonstrate whether wastes or reaction products might adversely affect the injection zone or confining zone. Tests conducted for the waste stream at the DeLisle Plant indicate that no significant compatibility problems exist. In addition, over 37 years of safe operations with no formation plugging or degradation problems are the most telling indicator that no problem exists.

6.2.1 Washita-Fredericksburg Fluid Analysis

Table 6-5 is an analysis of a native fluid sample from the Washita-Fredericksburg Sand formation fluid taken from Monitoring Well No. 1 recovered prior to beginning injection operations in 1974:

Table 6-6 is an analysis of a native fluid sample from the Washita-Fredericksburg Sand formation fluid taken from Injection Well No. 5 in 1994.

6.2.2 Formation Compatibility with Iron Chloride Waste

Halliburton conducted tests with various concentrations of ferric chloride ($FeCl_3$) waste on core samples obtained from Monitoring Well No. 1 (Halliburton, 1974). The tests were designed to determine whether the disposal fluid would permeate or degrade the shale confining layers.

Various compatibility tests with portions of the confining Washita-Fredericksburg shale taken from a depth of 9,663 feet were conducted. Waste concentrations of 15, 25, and 30 percent solution $FeCl_3$ were used with the waste at room temperature and atmospheric pressure for three hours. Some effervescence was observed, but the core pieces remained whole and intact, with only a small amount of fines released in each of the solutions. Halliburton's immersion tests using plant waste and shale indicated no unconsolidation of the shale. Direct flow tests using plant waste indicated that the shale is impervious and dense to fluid invasion. Thus it was demonstrated that the waste solution does not destroy the integrity of the shale layers nor their ability to isolate and confine waste fluid within the Washita-Fredericksburg Sand formation.

6.3 Well Materials Compatibility

Well material compatibility tests ensure that the materials in the well are compatible with the fluid with which they will come into contact. Properly selected materials of construction should minimize and mitigate corrosion, reduce maintenance and repairs, and provide for a well design that will operate safely and protect human health and the environment.

For conversion of Well No. 1 into an injection well (see Figures 5-2a and 5-2b), and for construction of future wells Nos. 6 and 7 (Figures 5-17 and 5-19), Chemours intends to use WellLock^{TM} resin instead of Epseal® resin. Appendix 6-4 is a letter dated October 31, 2013 providing responses to EPA Region 4 questions on the use of WellLock^{TM} resin, and the replacement of the FRP (fiberglass reinforced pipe) transition joint in the protective casing of the wells with a Hastelloy C276 transition joint. This makes for a more robust well design. Appendix 6-4 shows the results of tests demonstrating the compatibility of WellLock^{TM} resin with DeLisle iron chloride waste. Appendix 6-4 also contains the material data sheets for the WellLock^{TM} system components (resin, hardener and microsand). The WellLock^{TM} system was approved by EPA Region 4 for use in the construction of Well No. 6 with the issuance of the January 23, 2015 modification to the HWDIR.

6.3.1 Fiberglass Tubing Properties

A series of mechanical tests and visual observations were made to determine the effect of the liquid waste and well operation on the properties of the Fiberglass Reinforced Pipe (FRP) injection tubing (Cooney, 1981). The tubing was obtained from Well No. 3 and had been in service approximately eight months. The results of the tests are:

- Axial strength of joined tubing sections is in excess of 90 percent of original values;
- Resistance to crushing loads, applied normally to the longitudinal axis of the tube, is nearly 100 percent of original values; and
- The interior of the tubing showed no evidence of fatigue cracking or change in hardness.

Fiberglass reinforced tubing is an accepted industry material of construction for a highly acidic waste stream and has proven itself over years of trouble-free operations at the DeLisle Plant.

6.3.2 Effect of Tubing Scale on *Epseal*™ Cement Set Time

Because *Epseal*™ cement is used in the parts of the wellbore between casing and tubing and casing and the formation, it is necessary to know that the *Epseal*™ has set correctly. During cementing operations, there is a possibility that *Epseal*™ cement can flash or set too quickly. Laboratory tests were conducted to determine if scale on the interior of the tubing could possibly cause *Epseal*™ to flash set (Halliburton, 1980). Four sections of tubing were cut into eight-inch sections. Two sections were tested as received. The interiors of the other two were sand blasted and filled with 15 percent HCl. Rubber stoppers were placed in the bottoms of the tubing sections, and the sections were put into a 120°F water bath. The tubes were then filled with Epseal™. Tecam gel timers were used to determine the time at which each sample gelled. Results demonstrate that there was very little difference between the *Epseal*™ set times in tubing with interior scale and tubing without interior scale. Therefore, interior tubing scale poses no significant problem when cementing with Epseal™.

6.3.3 Effect of Ferric Chloride on Cements

Halliburton tested a variety of cement types for compatibility with $FeCl_3$ waste effluent (Halliburton, 1978). The cement slurries were cured for three days underwater at room temperature before complete immersion into the waste effluent sample. Every seven days the specimens were weighed and inspected, and the effluent was replaced with a fresh sample. These tests were conducted in sealed containers at room temperature for a duration of 28 days. Weight loss was calculated to show the initial weight loss and the loss at each time the samples were weighed. The types of cement tested and a summary of the results are shown in Table 6-7. All of the cement compositions tested except the *Epseal*™ showed significant deterioration and high weight loss by the end of the 28-day period of exposure to the waste sample. The *Epseal*™ slurry had practically no weight change and showed no visible signs of deterioration. *Epseal*™ is the cement used for all of those parts of the borehole which directly contact the waste stream.

Halliburton has recently developed WellLock™, an epoxy resin blend, as an alternative to Epseal™ cement for applications where the protection casing may be exposed to potentially corrosive formation fluids. One advantage of WellLock™ over Epseal™ is that it hardens in an aqueous medium whereas Epseal™ requires that all water be replaced with a non-aqueous medium (such as diesel oil) to achieve adequate setting. Therefore, it is easier to provide an effective annular barrier against potential upward fluid flow between the protection casing and the natural strata around it (i.e., avoid channeling and micro annuli). The mechanical properties of WellLock™ resin such as density, elasticity, and strength can be tailored to provide an effective annular corrosion barrier to protect the protection casing for specific well designs.

WellLock™ resin is not a cement system. On the contrary, the Poisson's ratio of WellLock™ resin is closer to that of rubber, whereas cement is closer to that of glass. In other words, cement is inherently stiff and this resin is inherently flexible. Some formulations of WellLock resin have achieved compressive strength of up to 48,500 psi. The shear bond strength of cement is generally 10% of the compressive strength (100-900 psi); and the shear bond strength of WellLock resin is consistently above 1,000 psi. Significantly, when pumped ahead of cement, a film of WellLock™ resin is left behind on the formation and outer diameter of the casing and can increase the shear bond strength of cement up to six-fold (6X).

Transition of WellLock™ resin from a liquid to a solid is another difference. The transition involves formation of covalent bonds via cross-linking reaction that initially builds viscosity, and the resin continues to transmit hydrostatic pressure to the formation. Importantly, at the cross-over point a non-porous three-dimensional network begins to form, the resin continues to transmit hydrostatic pressure to the formation until an impermeable barrier of cured resin forms. One foot of resin has been observed to resist a pressure differential of 1,000 psi. Both the cross-linked molecules and continuous transfer of hydrostatic pressure throughout the set time create a resistance to liquid or gas channeling.

This resin is resistant to acid, base, salts, and hydrocarbons. The temperature range of WellLock resin is 60°F-200°F (16°C-93°C) BHCT (bottom hole circulating temperature), up to 250°F (121°C) for BHST (bottom hole static temperature).

Chemours would like to use WellLock™ resin as an alternative to Epseal™ cement for Well Nos. 6 and 7; and for the conversion of Well No. 1 to an injection well. Refer to Appendix 6-4.

6.3.4 Coupon Corrosion Tests (1992 - 1995)

Continuous coupon corrosion tests have been in effect since early well operations. In 1992-1995 site data was compiled from quarterly corrosion monitoring of materials of well construction. Table 6-8 describes the results of this prolonged testing program. Results of three years of exposure to the injected waste of well materials, such as fiberglass and two different grades of titanium were collected. These data provide a conclusive indication that the waste stream is compatible with well materials. Table 6-9 provides these corrosion results using various well and tubular materials at ambient temperatures. Table 6-10 provides results of new testing performed on various well and tubular materials at 60° C conditions, and Table 6-11 provides corrosion testing results using various materials (Titanium) for 85° C conditions.

1. Fiberglass exposure with this test offered no evidence of corrosion present. This material is used as the injection tubing and in other piping and tubulars on site.
2. Titanium Grade 2 (with no Palladium content) corrosion coupons show a range of 0.00 to 0.08 mils per year (mpy) corrosion rates of Type 3; one mil is equal to one thousandth of one inch. This indicates only mild and superficial corrosion to the effects of the waste stream components.
3. Titanium Grade 7 (Ti – 0.15Pd) corrosion coupons show a range of 0.00 to 0.06 mpy corrosion rates of Type 3. This also indicates only mild and superficial corrosion to the effects of the waste. This construction material is found on the Groundwater Protection Services (GPS) injection packer and the injection casing present in all of the active wells.

In conclusion, with approximately 20 million gallons of waste exposure, essentially little or no corrosion was apparent in three years of continuous observations, monitoring, and reporting (Alexander, 1995).

6.3.5 Corrosion Tests on Titanium-Palladium (Ti-0.15Pd) Casing

Laboratory tests were conducted (Table 6-12) to determine the corrosion rate of Ti-0.15Pd casing (also known as Titanium Grade 7) in various concentrations of HCl, as well as its galvanic corrosion potential when in contact with carbon steel (Bovankovich, 1980). Ti-0.15Pd is the preferred material of construction for metallic well components in an acidic environment taking into account depth, temperature and pressure considerations.

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Hydrochloric Acid

The corrosion rate of Ti-0.15Pd casing was tested in various concentrations of HCl with a linear polarization resistance corrosion rate measuring instrument. The measured Ti-0.15Pd corrosion rate was one mpy at a concentration of 12 percent HCl. HCl concentration averages are three to five percent for the DeLisle waste stream, which means that the calculated corrosion rates are <1.0 mpy. Ti-0.15Pd casing corrosion rates tested significantly better than other similar construction materials, and Ti-0.15Pd casing is generally well within accepted industry standards.

6.3.6 Coupon Corrosion Tests (Historical)

A series of field and laboratory tests were conducted to determine the corrosion rates of various materials at different temperatures and over different periods of time when exposed to differing concentrations of waste stream constituents. The field corrosion results are shown in Tables 6-9 and 6-10. The laboratory results are shown in Tables 6-11 and 13 through 6-15. A brief description precedes the results of each test.

Test 1

The coupons were exposed for one month in a lamella settler (Kerns, 1981a). Typically, the ambient temperature waste stream composition was 80 percent ferrous and 20 percent ferric chloride for six days a week, and 30 percent ferrous for one day a week. In each case, the coupon was electrically insulated from the test plate. The results of this test are shown in Table 6-9.

Test 2

A coupon was exposed to the north lamella settler for two months (Kerns, 1981b). As in the first test, the waste stream was 80 percent ferrous and 20 percent ferric chloride for six days a week, and 30 percent ferrous for one day a week. The waste stream temperature was 60°C. In each case, the coupon was electrically insulated from the test plate. These results are shown in Table 6-10.

Test 3

Candidate alloys were lab tested for 35 days at 70° to 75°C in a solution containing five percent HCl and 15 to 20 percent iron chloride, consisting of 85 percent ferrous and 15 percent ferric iron (Kerns, 1981b). The results of this test are shown in Table 6-13.

Test 4

Laboratory corrosion tests were conducted on three titanium grades of casing in plant waste samples (Kerns, 1981c). The 30-day exposure involved daily monitoring of the ferrous ion concentration, total iron, HCl, and temperature. The following variations occurred during the sampling and monitoring period:

Ferrous Iron	63 - 95%
Total Iron	79 - 150mg/L
Background HCL	4.5 - 5.5%
Temperature	70 - 75°C

The test results from this study are shown in Table 6-14.

Test 5

Laboratory corrosion tests were conducted on two titanium grades of casing in plant waste samples (Kerns, 1982a). The 31-day exposure involved daily monitoring of the ferrous ion concentration, total iron, HCl, and temperature. The following variations occurred during the sampling period:

Ferrous Iron	81 - 100%
Total Iron	127 - 170 mg/L
Background HCL	4 - 5.25%
Temperature	78 - 84°C

The test results from this follow-up study are shown in Table 6-15.

Test 6

Laboratory corrosion tests were conducted on three titanium grades of casing in plant waste samples (Kerns, 1982b). The 44-day exposure involved daily monitoring of the ferrous ion concentration, total iron, HCl, and temperature. The following variations occurred during this period:

Ferrous Iron	89 - 97%
Total Iron	50 - 81 mg/L
Background HCL	4.3 - 5.0%
Temperature	81 - 89°C

The test results of this study are shown in Table 6-11.

Test 7

Three types of titanium coupons were exposed in the north lamella settler for six months (Kerns, 1982a). No crevice corrosion existed, and all uniform corrosion rates were less than one mil per year. The temperature was 55° to 60°C. The results are shown in Table 6-16.

Test 8

Laboratory corrosion tests were conducted to examine potential materials to replace Ti-0.15Pd casing currently used for metallic well components. The specific objective of the test was to measure three substitute candidate materials: Haynes Alloy C-22, Hastelloy C-276, and Ti-0.15Pd, under conditions expected during injection (Eyre, 1989).

Haynes Alloy C-22 and Hastelloy C-276 experienced corrosion rates in excess of 100 mpy when exposed to plant waste injection fluid. They are therefore deemed unsuitable for metallic construction components. Ti-0.15Pd casing exhibited corrosion rates of <5.0 mpy. In addition, no localized corrosion was detected in any of the autoclave experiments (Eyre, 1989). Thus, at reservoir conditions (approximately 230°F), Ti-0.15Pd has been determined to be the best material of construction available. For all metallic components which come in contact with the waste stream at DeLisle, this is the material used.

6.3.7 Corrosion-Rate Results from Measurements Required by MDEQ Permit MSI1001 Part I Section C.5

The results of corrosion measurements required by MDEQ Permit MSI1001 Part I Section C.5 are provided in Appendix 6-5.

6.3.8 Galvanic Corrosion Tests

Galvanic Corrosion in Inhibited Calcium Chloride Brine (Annulus Fluid)

Ti-0.15Pd was coupled to carbon steel and immersed in 36 percent inhibited $CaCl_2$ brine at 95°C to determine the steady state galvanic corrosion rate of carbon steel under these conditions. The current density measured was 0.0045 mA/cm^2, which converts to a corrosion rate of 2.06 mpy. Of significance is the fact that the electrodes were of equal surface area. Carbon steel was the anode and Ti-0.15Pd was the cathode in this situation. Under downhole conditions of temperature and pressure in the well, the effective cathode/anode surface area ratio is less than one, providing a more favorable ratio.

Additional Testing

Tests were conducted to determine whether the injection fluid contaminants caused an increase in the general corrosion rate or whether galvanic corrosion was inherent in a steel/titanium coupling (Cortest Laboratories, 1987).

Following are the four experimental tasks and the results:

1. Acidity measurements were conducted to determine the effect of inhibitor additions on solution pH. The results indicate that adding inhibitors has little, if any, significant effect on pH.
2. Polarization curves were measured for N80 and Ti electrodes. Only the anodic branch of the polarization curve was measured for the N80 electrode, and only the cathodic branch was measured for the Ti electrodes. The curves were essentially identical, indicating that the inhibitor has little effect on cathodic processes.
3. Galvanic current measurements were taken with a zero-resistance ammeter. The results indicate that when coupled to steel, the Ti electrodes are polarized to essentially the corrosion potential of steel. Thus, a maximum current density of two µmilsA/cm^2 can be estimated. The inhibitor does not appear to alter the galvanic corrosion current.
4. Polarization resistance measurements were obtained to determine the corrosion rate of uncoupled steel as a function of inhibitor concentration. The results do not indicate any dependence of corrosion rate on inhibitor concentration.

In subsequent discussion between the testing company (Cortest, 1987) and DuPont, it was concluded that corrosion during service could be attributed to one of the following two possibilities: localized corrosion at the Ti-0.15Pd/N-80 junction was galvanic but was accelerated by contamination of the packer fluid with waste injection fluid, or localized corrosion was galvanic and attributable to the well design (i.e., casing geometry, packer fluid, etc.) but not directly caused by waste fluid contamination.

Two types of experiments were conducted. In the first type, coupons of steel and Ti were coupled and exposed to the packer fluid environment (varying surface areas of steel and Ti in the coupled coupon pairs) to measure the effect of anode/cathode surface area ratio on galvanic corrosion. Results indicated that corrosion rates of all coupons were <2.0 mpy. Galvanic influence to corrosion is roughly 50 percent. These experiments also indicated that small geometry experiments may not adequately reproduce galvanic action experienced in actual service.

In the second type, experiments involved modeling the pipe configuration such that galvanic currents could be measured using a geometry that approximated the well configuration. Modeling results included the observation that cathodic currents are generated on steel surfaces as well as Ti surfaces. The magnitude of galvanic current is lower (by a factor of 10) than that required to account for field observations.

Additional results of this study indicated that contamination of packer fluid by waste solution increased the galvanic current density on Ti by a factor of two, but eliminated the galvanic contribution of passive steel. The exact cause of galvanic corrosion experienced during service is not known. However, it appears that no contamination of the packer fluid by waste fluid has occurred. Therefore, such contamination is not responsible for the corrosion effects experienced in service (Cortest, 1987).

6.3.9 2011 and 2012 Corrosion Testing

An FRP transition piece is used in Wells Nos. 2, 3, 4 and 5 to isolate the carbon steel portion of the protection casing from the Titanium Grade 7 portion below. However, the FRP transition piece makes it difficult to rework the wells, and to maintain their ability to accept an appropriate waste flow rate. Replacing the FRP with metal will increase the pressure rating of the protection casing, and provide additional operational flexibility.

Corrosion testing was performed in 2011 and 2012 (Saldanha & Eyre, 2012) to determine whether the existing FRP transition piece can be eliminated, or substituted with a metallic transition piece. In addition to measuring galvanic effects, the testing also was designed to determine whether Titanium Grade 7 would be embrittled by the formation of Titanium hydrides. This test was done over a 12-week period in plant-supplied inhibited 36% CaCl2 brine at 108°C and 127°C. Testing at 127°C was intended to represent the maximum temperature the transition joint is expected to experience.

The testing also sought to identify if other grades of titanium provide corrosion resistance comparable to Titanium Grade 7, but at more competitive costs and better availability. For this purpose, coupons of Titanium Grade 7 (Ti – 0.15Pd) and Titanium Grade 16 (Ti – 0.05Pd) were exposed to static crevice corrosion tests, both short-term and longer-term in plant-supplied 36% $CaCl_2$ brine over more than 8 weeks at both 108°C and 127°C. The intent was to compare the susceptibility of these two alloys to hydrogen uptake and crevice corrosion.

Results of Galvanic Corrosion Tests

No appreciable galvanic corrosion effect was measured when coupling Titanium Grade 7 and carbon steel in 36% $CaCl_2$ at the elevated temperatures representative of conditions at the bottom of the well. Various area rations of carbon steel to Titanium Grade 7 coupons were exposed to 36% $CaCl_2$ inhibited brine at atmospheric-boiling temperature (108°C) for 8 weeks. A separate group of coupons was exposed to maximum temperature of 127°C for 4 weeks, and another group was exposed for 12 weeks. Test data is summarized in Table 6-17.

Key observations are:

1. Corrosion rates of both Titanium Grade 7 and carbon steel decreased with exposure time to less than 1 mpy for both metals. The Titanium Grade 7 showed no crevice attack.
2. The low rates on steel suggest that the additives in the brine (corrosion inhibitors and oxygen scavengers) appear to be effective in controlling corrosion of steel to 1 mpy or less.
3. Over the longer exposures, there was no obvious increase in corrosion of steel (or decrease in corrosion of Titanium Grade 7) as a result of galvanically coupling these two alloys over a range of surface ratios from 4:1 to 1:1 to 1:4 to un-coupled.
4. Representative coupons of Titanium Grade 7 were analyzed for hydrogen uptake and hydride microstructures. There was no obvious hydrogen uptake or evidence of hydrides in microstructures.

Identification of Suitable Substitutes to Titanium Grade 7

Titanium Grade 16 and Titanium Grade 7 coupons were exposed to iron chloride waste from the DeLisle Plant. One group of coupons was exposed to atmospheric boiling conditions (108°C) for 5 days. A separate group of coupons was exposed to maximum temperature conditions (127°C) for 6 weeks, and another group of coupons was exposed to this temperature for 12 weeks.

The corrosion data is summarized in Table 6-18. Key observations are:

1. Crevice attack was not observed on any of these alloys, and their corrosion rates were low and comparable to each other. In fact, there was a slight weight gain on all the Titanium alloys in the 12-week test. This suggests that the Titanium Grade 16 should be an effective replacement for Titanium Grade 7.
2. Representative coupons of these titanium alloys were tested to determine the rate of hydrogen uptake, and the presence of hydride microstructures. There was no evidence of hydrides in the microstructures after 12 weeks of exposure.

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TABLES

Table 6-1

Classical Chemistry Parameters of the Waste Stream

Parameter	Result	Method Reporting Limit (MRL)	Units	Method
Classical Chemistry Parameters				
Cyanide (total)	Non-detect (ND)	0.039	mg/kg	SM 4500-CN E 1999
Chloride	146,000	23,600	mg/kg	EPA 300.0
Viscosity @ 70C	0.972		centi Stokes	
Fluoride	ND	0.150	mg/kg	SM 4500-F D 1997
Total Dissolved Solids	158,300	1	mg/kg	SM 2540C 1997
Sulfite	15.0	3.28	mg/kg	SM 4500-SO3 2-B 2000
Phosphorus, Total	47.2	5.64	mg/kg	SM 4500-P B5; SM 4500-P E
Bromide	ND	159	mg/kg	EPA 300.0
Nitrate as N	ND	34.5	mg/kg	EPA 300.0
Sulfate as SO4	ND	73.0	mg/kg	EPA 300.0
Acidity	197,000	1	mg/kg	SM 2310B 1997
pH	-0.37		pH units	SW 846 9040
Specific Gravity	1.213		g/ml	SM 2710F (room temperature)
Total Organic Carbon	ND	7.44	mg/kg	SM 5310C 2000
Total Suspended Solids	3.5	1	mg/kg	SM 2540D 1997

Table 6-2

Radiochemistry Parameters of the Waste Stream

Radiological Parameters				
Analysis Description	Result	Minimum Detectable Concentration (MDC)	Units	Method
Th-232	5607.955	100.517	pCi/L	ARS-031/Eichrom ACW-10
U-238	1386.717	16.414	pCi/L	ARS-026/Eichrom ACW-03
Be-7	53.849	88.500	pCi/L	ARS-006/EPA 901.1
Bi-212	3898.600	82.300	pCi/L	ARS-006/EPA 901.1
Bi-214	747.540	22.700	pCi/L	ARS-006/EPA 901.1
Pa-234	169.920	29.900	pCi/L	ARS-006/EPA 901.1
Pb-210	1443.800	195.000	pCi/L	ARS-006/EPA 901.1
Pb-214	840.990	24.900	pCi/L	ARS-006/EPA 901.1
Ra-226	2715.600	246.000	pCi/L	ARS-006/EPA 901.1
Ra-228	5388.400	29.500	pCi/L	ARS-006/EPA 901.1
Sc-46	-5.017	6.100	pCi/L	ARS-006/EPA 901.1
Th-228	6062.700	26.000	pCi/L	ARS-006/EPA 901.1
Tl-208	1969.100	11.900	pCi/L	ARS-006/EPA 901.1
U-235	27.972	83.500	pCi/L	ARS-006/EPA 901.1
Total NORM Gamma	31146.621	N/A	pCi/L	ARS-006/EPA 901.1
Total NORM Activity	53534.089	N/A	pCi/L	ARS-006/EPA 901.1

Table 6-3

Metals Analysis of the Waste Stream

Analyte	Result	Method Reporting Limit (MRL)	Units	Method
Silicon	33.4	2.49	mg/kg	EPA 6010
Aluminum	1520	2.49	mg/kg	SW 6010
Antimony	ND	2.49	mg/kg	SW 6010
Arsenic	ND	2.49	mg/kg	SW 6010
Barium	31.5	0.498	mg/kg	SW 6010
Beryllium	ND	0.199	mg/kg	SW 6010
Boron	5.97	2.49	mg/kg	SW 6010
Calcium	74.8	2.49	mg/kg	SW 6010
Chromium	896	0.498	mg/kg	SW 6010
Cobalt	16.7	2.49	mg/kg	SW 6010
Copper	3.77	0.498	mg/kg	SW 6010
Lead	69.8	2.49	mg/kg	SW 6010
Magnesium	727	2.49	mg/kg	SW 6010
Potassium	33.6	14.9	mg/kg	SW 6010
Nickel	3.33	2.49	mg/kg	SW 6010
Selenium	3.33	2.49	mg/kg	SW 6010
Silver	2.44	0.249	mg/kg	SW 6010
Sodium	3,500	4.98	mg/kg	SW 6010
Strontium	6.45	2.49	mg/kg	SW 6010
Thallium	ND	2.49	mg/kg	SW 6010
Titanium	1,330	2.49	mg/kg	SW 6010
Vanadium	378	2.49	mg/kg	SW 6010
Zinc	83.7	0.995	mg/kg	SW 6010
Cadmium	ND	4.74	mg/kg	SW 6010
Iron	74,000	23.7	mg/kg	SW 6010
Manganese	3,550	23.7	mg/kg	SW 6010
Ferric Ion	ND	1,170	mg/kg	EPA 6010
Ferrous Ion	74,000	1,170	mg/kg	EPA 6010

Table 6-4

Historical Data Ranges of Waste Stream Analytes

(for Three Calendar Years ending in March 2016)

Parameter	Appendix 6-3 Value	Units	Analytical Method	Method Reporting Limit (MRL)	Historical Range
Iron	74,000	mg/kg	SW 6010B	25	64,300 - 94,000
Chromium	898	mg/kg	SW 6010B	5	710 – 2,000
Vanadium	378	mg/kg	SW 6010B	25	314 – 484
Lead	69.8	mg/kg	SW 6010B	25	65 – 96
Chloride	146,000	mg/kg	SM 4110B 2000	24,000	170,000 – 450,000
Total Organic Carbon	ND	mg/kg	SM 5310C 2000	4.36 – 7.44	Always < (less than) MRL
Acidity	197,000	mg/kg	SM 2310B 1997	1	192,000 – 251,000
Specific Gravity	1.213	mg/L	SM 2710F		1.200 – 1.257

Table 6-5

Washita-Fredericksburg Formation Fluid Analysis (Monitoring Well No. 1 -- 1974)

Constituent	Concentration (mg/L)
Calcium	10,000 - 20,000
Sodium	40,000 - 60,000
Chlorides	80,000 - 95,000
Sulfates	100 - 300
Iron	1.0 - 1.5
Magnesium	1,000 - 1,500
Bromine	600 - 1,000
Manganese	10 - 20
pH	6.3 - 6.8

Table 6-6

Washita-Fredericksburg Formation Fluid Analysis (Well No. 5 -- 1994)

Constituent	Concentration	Units
Barium	4.3	ppm
Cadmium	0.007	ppm
Strontium	4.5	ppm
Nitrate	< 0.1	mg/L
Chloride	71,750	ppm
Cyanide	< 0.1	mg/L
Density	1.085	g/cc
Fluoride	0.42	mg/L
Phosphate (Total)	< 0.05	mg/L
Sulfate	131	mg/L
Sulfite	< 10	mg/L
Total Dissolved Solids (TDS)	105,000	ppm
Total Suspended Solids (TSS)	1,608	ppm
Bromide	546	mg/L
Carbonate	199	ppm

Table 6-7
Effect of Ferric Chloride on Cements

Cement Sample	Effluent Solution (pH)	Weight Loss (%)	Notes*
Latex Class A + 0.9 gal LA-2	0.80	17.35	1, 2, 3
Latex Class A + 0.9 gal LA-2 + NF1	0.75	23.05	1, 2, 3
Latex Class A + 1.8 gal LA-2	0.75	18.76	1, 2, 3, 6
Latex Class A + 1.8 gal LA-2 + NF1	0.75	22.64	1, 2, 3, 6
Pozmix A + 1.8 gal LA-2	0.45	16.44	2, 4, 6
Pozmix A + 1.8 gal LA-2 + NF1	0.55	22.49	2, 4, 6
Pozmix A + 1.0% CFR-2	0.75	19.70	2, 4, 7, 8
Pozmix A + 1.0% CFR-2 +NF1	0.70	23.82	2, 3, 4
Epseal™	0.05	+00.14	
API Class A + 0.9 gal MC76 acrylic	0.45	11.20	1, 9
API Class A + 1.8 gal MC76 acrylic	0.25	11.99	1, 9
Pozmix A + 1.8 gal E330 acrylic	0.30	11.75	2, 9
Pozmix A + 4.04 gal E330 acrylic	0.30	9.68	
Pozmix A + 7.82 gal E330 acrylic	0.25	8.61	
API Class C	0.50	8.88	1, 2, 10
API Class H	0.50	8.17	1, 9
API Class H + 0.9 gal MC76 acrylic	1.0	10.15	1

* After 28 days, rinsed 1 hour, sprayed and blotted

Notes:

1	Yellow color
2	Soft surface
3	Surface blisters
4	Dark gray color
5	Center firm after sample was scrubbed
6	Rounding corners
7	Chipping corners
8	Surface flaking
9	Gray film
10	Some surface corrosion

Reference: Halliburton, 1978

Table 6-8

1992 - 1995 Coupon Corrosion Data

Material	Corrosion Rates (mpy)	Type	Notes
Fiberglass	No corrosion	NA	Slight discoloration
Titanium Grade 2	0.00 - 0.08	Type 3	Superficial corrosion
Titanium Grade 7	0.00 - 0.06	Type 3	Superficial corrosion

Table 6-9

Field Corrosion Results at Ambient Temperature

Material	Corrosion Rate	Comments
Titanium Grade 2	0.065 mpy	Uniform corrosion
Titanium Grade 2	0.080 mpy	Uniform corrosion
TiCode 12	0.14 mpy	Uniform corrosion
TiCode 12	0.12 mpy	Uniform corrosion
Hastelloy C-276	0.80 mpy	Uniform corrosion
Hastelloy C-276	0.82 mpy	Crevice corrosion
Ti-Pd	0.14 mpy	Uniform corrosion
Ti-Pd	0.13 mpy	Uniform corrosion
Inconel 625	missing	
Inconel 625	missing	
Admiralty brass	missing	
Admiralty brass	missing	

(Tests conducted in 1981)

Table 6-10

Field Corrosion Results on Various Materials at 60°C

Material	Corrosion Rate	Comments
Titanium Grade 2	0.024 mpy	Uniform corrosion
Titanium Grade 2	0.013 mpy	Uniform corrosion
Titanium Grade 2	0.074 mpy	Uniform corrosion
TiCode 12	nil	
TiCode 12	0.050 mpy	Uniform corrosion
TiCode 12	0.041 mpy	Uniform corrosion
Hastelloy C-276	4.87 mpy	Uniform corrosion
Hastelloy C-276	2.24 mpy	Crevice corrosion
Ti-Pd	0.064 mpy	Uniform corrosion
Ti-Pd	0.031 mpy	Uniform corrosion
Ti-Pd	0.002 mpy	Uniform corrosion
Inconel 625	missing	
Inconel 625	missing	
Admiralty brass	missing	
Admiralty brass	missing	
Inconel 600	missing	
Inconel 600	missing	

(Tests conducted in 1981)

Table 6-11

Laboratory Corrosion Tests on Various Materials at 85°C

Material	Corrosion Rate	Comments
Titanium Grade 7 (Ti-Pd)	0.10 mpy	Uniform corrosion
Titanium Grade 7 (Ti-Pd)	0.07 mpy	Very minor crevice corrosion
Titanium Grade 2	0.52 mpy*	Severe crevice corrosion
Titanium Grade 2	4.16 mpy*	Severe crevice corrosion
TiCode 12	0.08 mpy	Crevice corrosion
TiCode 12	0.18 mpy	Crevice corrosion

* This rate calculation reflects only metal loss due to severe crevice corrosion

(Tests conducted in 1981)

Table 6-12

Corrosion Rate Summary
Titanium-0.2Pd (Titanium with 0.2% Palladium)
Corrosion Rates in Millimeters per year at 50°C

% HCl	Corrosion
4	0.6
12	1
20	24
28	<1,000
36	<1,000

(Tests conducted in 1980)

Table 6-13

Laboratory Corrosion Tests on Various Materials at 70° to 75°C

Material	Corrosion Rate	Comments
Titanium Grade 2	14.0 mpy	Crevice corrosion, pitting
TiCode 12	60.4 mpy	Pitting
Hastelloy C-276	10.3 mpy	Severe crevice corrosion
Ti-Pd	0.13 mpy	Uniform corrosion
Inconel 625	233 mpy	Severe end grain attack
Inconel 600	255 mpy	Pitting, crevice corrosion, severe end grain attack
Inconel 600	253 mpy	Pitting, severe end grain attack

(Tests conducted in 1981)

Table 6-14

Laboratory Corrosion Tests on Various Materials at 70°C

Material	Corrosion Rate	Comments
Titanium Grade 2	0.12 mpy	Crevice corrosion
Titanium Grade 2	0.34 mpy	Crevice corrosion
Titanium Grade 7 (Ti-0.15Pd)	0.028 mpy	Uniform corrosion
Titanium Grade 7 (Ti-0.15Pd)	No data	Uniform corrosion
TiCode 12	0.029 mpy	Uniform corrosion
TiCode 12	0.047 mpy	Uniform corrosion

(Tests conducted in 1981)

Table 6-15

Laboratory Corrosion Tests on Various Materials at 80°C

Material	Corrosion Rate	Comments
Titanium Grade 7 (Ti-Pd)	0.05 mpy	Uniform corrosion
Titanium Grade 7 (Ti-Pd)	0.06 mpy	Uniform corrosion
TiCode 12	0.44 mpy	Very mild pitting
TiCode 12	0.07 mpy	Very mild pitting

(Tests conducted in 1981)

Table 6-16

Lamella Settler Corrosion Tests

Material	Corrosion Rate	Comments
Titanium Grade 7 (Ti-Pd)	0.043 mpy	Uniform corrosion
Titanium Grade 7 (Ti-Pd)	0.052 mpy	Uniform corrosion
Titanium Grade 2	0.035 mpy	Uniform corrosion
Titanium Grade 2	0.047 mpy	Uniform corrosion
TiCode 12	0.042 mpy	Uniform corrosion
TiCode 12	0.036 mpy	Uniform corrosion

(Tests conducted in 1982)

Table 6-17

Summary of Galvanic Corrosion Tests for Titanium Grade 7 and Carbon Steel

Table I: 36% CaCl2 - Corrosion Data at 108°C (Atmosspheric) and at 127°C (Autoclave Conditions)
(Supplied by Delisle with Inhibitros and Oxygen Scavengers); Initial pH 8.4

Carbon Steel coupled to Titanium with various area ratios: 0, 1:4, 1;1, and 4;1		127°C Autoclave (Static)								Boiling (108°C) Static - Test Tubes				Boiling (108°C) Static Resin Kettle		Boiling (108°C) 150 rpm Resin Kettle	
		1985 Hours Final pH: 8.0 Pressure: 33psi			672 Hours Final pH: 8.0 Pressure: 33psi			168 Hours Final pH: 8.1 Pressure: 34		1344 Hours Final pH: 7.5		572 Hours Final pH: 7.5		144 Hours Final pH: 7.9		144 Hours Final pH: 7.9	
Alloy	ID No.	Corrosion Rate (mpy)	Max Crevice Depth (mils)	Max Pit Depth (mils)	Corrosion Rate (mpy)	Max Crevice Depth (mils)	Max Pit Depth (mils)	Corrosion Rate (mpy)	Max Crevice Depth (mils)	Corrosion Rate (mpy)	Max Crevice Depth (mils)	Corrosion Rate (mpy)	Max Crevice Depth (mils)	Corrosion Rate (mpy)	Max Crevice Depth (mils)	Corrosion Rate (mpy)	Max Crevice Depth (mils)
1018 Carbon Steel	Not Coupled	0.3	3		0.9	3	2	5.1	2	0.0	2	0.3	3	0.6		1.3	3
		0.3	3		1.1	3	2	6.4	2	0.1	2	0.4	2				
	(CS:Ti7 ratio 1:4)	0.3	2		1.0	2	1	3.8	2	0.3	4	0.5	2	2.3		3.1	2
		0.5	2		1.0	3	2	3.9	2	0.2	3	0.4	1				
	(CS:Ti7 ratio 1:1)	0.7	7	3	0.9			3.5	2	0.3	4	0.9	2	1.8	1	2.1	2
										0.3	3	0.7	2				
	(CS:Ti7 ratio 4:1)	0.4	4		0.9	1		4.2	2	0.1	3	0.3	1				
		0.3	3		0.9	3	1	4.5	2	0.1	4	0.3	3				
										0.1	4	0.3	3				
										0.1	4	0.3	1				
Titanium Grade 7	Not coupled	0.04			0.12			0.53		0.00		0.06					
										0.00		0.06					
	(CS:Ti7 ratio 1:4)	0.04			0.07			0.29		0.02		0.00		0.00		0.29	
		0.03			0.05			0.35		0.03		0.02		0.05		0.09	
		0.02			0.10			0.31		0.01		0.01					
		0.03			0.09			0.37		0.02		0.01					
	(CS:Ti7 ratio 1:1)	0.03			0.08			0.37		0.01		0.02		0.00		0.14	
										0.00		0.01					
	(CS:Ti7 ratio 4:1)	0.02			0.06			0.27		0.00		0.01					
										0.01		0.01					

Table 6-18

Comparison of Titanium Grade 7 and Titanium Grade 16 Corrosion Exposed to DeLisle Iron Chloride

Table II: Coupon Data: 24% Ferrous Chloride, 1.3% Ferric Chloride, Balance Water

Alloy			Corrosion Rate (mpy)		
Designation (UNS, DIN)	Common Alloy Name	Coupon Condition	108C 118 Hours	127C 1008 Hours	127C 1992 Hours
R50400	Titanium Gr 2	Mill Finish, Flat Washer, Multiple Crevice Washer	**0.31**		
R50400	Titanium Gr 2	Mill Finish, Flat Washer, Multiple Crevice Washer	**0.31**		
R52400	Titanium Gr 7	Mill Finish, Flat Washer, Multiple Crevice Washer	**0.35**	**(0.04)**	**(0.16)**
R52400	Titanium Gr 7	Mill Finish, Flat Washer, Multiple Crevice Washer	**0.22**	**(0.02)**	**(0.04)**
R52402	Titanium Gr 16	Mill Finish, Flat Washer, Multiple Crevice Washer	**0.28**	**(0.05)**	**(0.03)**
R52402	Titanium Gr 16	Mill Finish, Flat Washer, Multiple Crevice Washer	**0.25**	**(0.04)**	**(0.01)**
R52404	Titanium Gr 26	Mill Finish, Flat Washer, Multiple Crevice Washer	**0.53**		
R52404	Titanium Gr 26	Mill Finish, Flat Washer, Multiple Crevice Washer	**0.48**		

APPENDICES

APPENDIX 6-1
ANALYTICAL REPORT FOR IRON CHLORIDE MONTHLY COMPOSITE SAMPLE

MICRO-METHODS
LABORATORY, INC.

Mailing Address:
PO Box 1410
Ocean Springs, MS
39566-1410

6500 Sunplex Drive
Ocean Springs, MS 39564
228.875.6420 Phone
228.875.6423 Fax

March 15, 2016

Ed Ramos

Work Order # : 1603093

The Chemours Company FC LLC
974 Centre Rd.
Wilmington, DE 19805

Purchase Order #: 9900007395

RE: Environmental Deepwell

Enclosed are Micro-Methods Laboratory, Inc. results of analyses performed on samples received 03/03/16 12:50. If you have any questions concerning this report, please feel free to contact the office.

Sincerely,

Harry P. Howell

Harry P. Howell

President
Micro-Methods Laboratory, Inc.

DISCLAIMER

The results only relate to the items or the sample and/or samples received by the laboratory. This report shall not be reproduced except in full, without the approval of the laboratory. All test methods performed meet the requirements of NELAC 2009 Standards. Any variances and/or deviations specific to this analytical report are referenced in the lab report using qualifiers and detailed explanations found in the case narrative.

The Chemours Company FC LLC
974 Centre Rd.
Wilmington DE, 19805

Project: Environmental Deepwell
Project Number: [none]
Project Manager: Ed Ramos

Reported:
03/15/16 08:35

ANALYTICAL REPORT FOR SAMPLES

Sample ID	Laboratory ID	Matrix	Date/Time Sampled	Sampled by	Date/Time Received
Environmental Depwell 4978795	1603093-01	Liquid	03/03/16 08:00	*J. Raskett*	03/03/16 12:50

Sample Receipt Conditions

Date/Time Received: 3/3/2016 12:50:00PM

Shipped by: Lab Pick-up

Received by: Sarah E. Tomek

Submitted by: Mike Farrell

Date/Time Logged: 3/3/2016 1:36:00PM

Logged by: Sarah E. Tomek

Cooler ID: client cooler

Receipt Temperature: 0.0 °C

Custody Seals	*No*	*Received on Ice*	*Yes*
Containers Intact	*Yes*	*No Ice, Short Trip*	*No*
COC/Labels Agree	*Yes*	*Obvious Contamination*	*No*
Labels Complete	*No*	*Rush to meet HT*	*No*
COC Complete	*Yes*		

CASE NARRATIVE SUMMARY

All reported results are within Micro-Methods Laboratory, Inc.defined laboratory quality control objectives unless detailed in narrative summary or identified as qualifications. NOTE: All results listed on this report are calculated on a wet weight basis (as received by the laboratory) unless otherwise noted in the analysis qualification sections.

Summary Comments: *No Summary Comments*

Total Metals-SW 6010B

Qualifiers:

L1 LCS and/or LCSD Recovery Limit exceeded.

Iron
6C08017-BSD1

L3 LCS/LCSD Precision Limit exceeded.

Iron
6C08017-BSD1

Environmental Depwell 4978795

1603093-01 (Liquid)

Analyte	Result	MRL	Units	Dil	Batch	Analyst	Date Time Prepared	Date Time Analyzed	Method	Qualifiers
Classical Chemistry Parameters										
Acidity	**218000**	1	mg/kg	1	6C04028	GMS	03/04/16 15:30	03/04/16 15:40	SM 2310B 1997	
Chloride	**200000**	24000	"	50000	6C03022	DLW	03/03/16 14:21	03/03/16 14:21	SM 4110B 2000	
Specific Gravity	**1.237**		g/mL	1	6C04027	GMS	03/04/16 15:15	03/04/16 15:25	SM 2710 F.	
Total Organic Carbon	ND	7.44	mg/kg	10	6C04023	DLW	03/04/16 13:44	03/04/16 13:44	SM 5310C 2000	
Total Suspended Solids	**7.3**	1.0	"	1	6C04025	DLW	03/04/16 12:00	03/04/16 15:42	SM 2540 D 1997	
Metals										
Chromium	**1150**	5.00	mg/kg	5	6C08017	SCH	03/08/16 08:50	03/11/16 14:28	SW 6010B	
Iron	**80400**	25.0	"	"	"	SCH	"	"	"	
Lead	**77.2**	25.0	"	"	"	SCH	"	"	"	
Vanadium	**439**	25.0	"	"	"	SCH	"	"	"	

Classical Chemistry Parameters - Quality Control

Batch 6C03022 - Default Prep GenChem

Blank (6C03022-BLK1) *Prepared & Analyzed: 03/03/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Chloride	ND	0.47	mg/kg							

LCS (6C03022-BS1) *Prepared & Analyzed: 03/03/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Chloride	3.6	0.47	mg/kg	4.00		90.5	75-125			

LCS Dup (6C03022-BSD1) *Prepared & Analyzed: 03/03/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Chloride	3.8	0.47	mg/kg	4.00		95.5	75-125	5.32	30	

Duplicate (6C03022-DUP1) **Source: 1603093-01** *Prepared & Analyzed: 03/03/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Chloride	200000	24000	mg/kg		200000			3.44	30	

Batch 6C04023 - Default Prep GenChem

Blank (6C04023-BLK1) *Prepared & Analyzed: 03/04/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Total Organic Carbon	ND	0.74	mg/kg							

LCS (6C04023-BS1) *Prepared & Analyzed: 03/04/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Total Organic Carbon	5.05	0.74	mg/kg	5.00		101	75-125			

LCS Dup (6C04023-BSD1) *Prepared & Analyzed: 03/04/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Total Organic Carbon	5.06	0.74	mg/kg	5.00		101	75-125	0.225	35	

Duplicate (6C04023-DUP1) **Source: 1603093-01** *Prepared & Analyzed: 03/04/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Total Organic Carbon	ND	7.44	mg/kg		ND				30	

Batch 6C04025 - Default Prep GenChem

Blank (6C04025-BLK1) *Prepared & Analyzed: 03/04/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Total Suspended Solids	ND	1.0	mg/kg							

Classical Chemistry Parameters - Quality Control

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Batch 6C04025 - Default Prep GenChem										
LCS (6C04025-BS1)						*Prepared & Analyzed: 03/04/16*				
Total Suspended Solids	83.0		mg/kg	100		83.0	75-125			
LCS Dup (6C04025-BSD1)						*Prepared & Analyzed: 03/04/16*				
Total Suspended Solids	83.0		mg/kg	100		83.0	75-125	0.00	25	
Duplicate (6C04025-DUP1)	**Source: 1603093-01**					*Prepared & Analyzed: 03/04/16*				
Total Suspended Solids	7.3	1.0	mg/kg		7.3			0.00	5	
Batch 6C04027 - Default Prep GenChem										
Duplicate (6C04027-DUP1)	**Source: 1603093-01**					*Prepared & Analyzed: 03/04/16*				
Specific Gravity	1.234		g/mL		1.237			0.251	200	
Batch 6C04028 - Default Prep GenChem										
Duplicate (6C04028-DUP1)	**Source: 1603093-01**					*Prepared & Analyzed: 03/04/16*				
Acidity	223000	1	mg/kg		218000			2.25	35	

Metals - Quality Control

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Batch 6C08017 - EPA 3010A										
Blank (6C08017-BLK1)					***Prepared: 03/08/16 Analyzed: 03/11/16***					
Chromium	ND	0.500	mg/kg							
Iron	ND	2.50	"							
Lead	ND	2.50	"							
Vanadium	ND	2.50	"							
LCS (6C08017-BS1)					***Prepared: 03/08/16 Analyzed: 03/11/16***					
Chromium	9.26	0.500	mg/kg	10.0		92.6	85-115			
Iron	9.45	2.50	"	10.0		94.5	85-115			
Lead	9.89	2.50	"	10.0		98.9	85-115			
Vanadium	10.4	2.50	"	10.0		104	85-115			
LCS Dup (6C08017-BSD1)					***Prepared: 03/08/16 Analyzed: 03/11/16***					
Chromium	9.07	0.500	mg/kg	10.0		90.7	85-115	2.03	20	
Iron	13.8	2.50	"	10.0		138	85-115	37.7	20	L1, L3
Lead	9.66	2.50	"	10.0		96.6	85-115	2.39	20	
Vanadium	10.4	2.50	"	10.0		104	85-115	0.357	20	
Duplicate (6C08017-DUP1)	**Source: 1603093-01**				***Prepared: 03/08/16 Analyzed: 03/11/16***					
Chromium	1220	4.98	mg/kg		1150			5.55	20	
Iron	83400	24.9	"		80400			3.66	20	
Lead	81.3	24.9	"		77.2			5.13	20	
Vanadium	459	24.9	"		439			4.43	20	

Certified Analyses Included in this Report

Analyte	Certification Code
SM 5310C 2000 in Liquid	
Total Organic Carbon	C01,C02

Laboratory Accreditations/Certifications

Code	Description	Number	Expires
C01	*La Environmental Lab Accreditation Program*	*01960*	*06/30/2016*
C02	*National Environmental Lab Accreditation Program*	*TNI01397*	*06/30/2016*
C03	*Ms Dept of Health (Coliform)*	*MS00021*	*03/15/2016*
C04	*Ms Dept of Health (Drinking Water Certificate)*	*MS00021*	*03/15/2016*
C05	*Ms DEQ Lead Firm Certification*	*PBF-00000028*	*11/11/2016*
C06	*MsDEQ Asbestos Inspector : C.D. Bingham*	*ABI-00001348*	*03/13/2016*
C07	*MsDEQ Air Monitor : C.D. Bingham*	*AM-011572*	*03/12/2016*
C08	*MsDEQ Asbestos Inspector: C. W. Meins*	*ABI-00001821*	*10/08/2016*
C09	*MsDEQ Air Monitor : C.W. Meins*	*AM-011189*	*03/12/2016*
C12	*MsDEQ Asbestos Inspector : H.P. Howell*	*ABI-00001345*	*03/14/2016*
C14	*MsDEQ Lead Paint Inspector : C.D. Bingham*	*PBI-00003690*	*04/20/2016*
C15	*MsDEQ Lead Paint Inspector : C.W. Meins*	*PBI-00001740*	*04/20/2016*

Report Definitions

TNC	Too Numerous To Count
DET	Analyte DETECTED
ND	Analyte NOT DETECTED at or above the minimum reporting limit
NR	Not Reported
RPD	Relative Percent Difference
ICV	Initial Calibration Verfiication
CCV	Continuing Calibration Verification Standard
SSV	Secondary Source Verfication Standard
LCS	Lab Control Spike - Lab matrix prepared with known concentration of analyte/s of interest analyzed by method.
MS	Matrix Spike - Sample prepared with known concentration of analyte/s of interest analyzed by method.
MSD	Matrix Spike Duplicate - Duplicate sample prepared with known concentration of anlayte/s of interest analyzed by method.
MRL	Minimum Reporting Limit
%REC	Percentage Recovery of known concentration added to matrix
Batch	Group of samples prepared for analysis not to exceed 20 samples.
Matrix	Material containing analyte/s of interest
Surrogate	Analyte added to sample to determine extraction efficiency of method.

Analyst Initials Key

FullName	Initials
Barbara K. McMillan	BKM
Dortha L. Wells	DLW
Gayle M. Sparling	GMS
Sarah E. Tomek	SET
Samantha C. Hall	SCH
Tina Tomek	TPT
Vye Steelman	VNS

Chemours Company – Delisle Plant
P. O. Box 430
Pass Christian, MS 39571
Ed Ramos (228) 255-4931

CHAIN OF CUSTODY RECORD

1603093

Sample Name DEEPWELL MONTHLY COMPOSITE						Number of Containers	Ppm Fe	Ppm Cr	Ppm V	Ppm Pb	Total Acicity	Total Organic Carbon	Total Suspended Solids	Specific Gravity	Mg/L Chlorides
Samplers Name(s) J. Raskett															
Sample No.	Date	Time	Comp	Grab	Sample Location										
4978795 Feb 2016	03/03/16	0800	✓		Env. Deepwells	1	✓	✓	✓	✓	✓	✓	✓	✓	✓

Released By: (Signature) James F. Raskett	Date and Time Released 3/3/16 @1100	Received By: (Signature)	Date and Time Received 3-3-16 @ 1100
Printed Name JAMES F. RASKETT		Printed Name Michael Farrell	
Released By: (Signature)	Date and Time Released 3-3-16@ 1250 ~~3-3-16@ 1100~~	Received By: (Signature) Sarah Tomek	Date and Time Received 3/03/16 @1250
Printed Name ~~Michael Farrell~~ Michael Farrell		Printed Name Sarah Tomek	

MCF
3-3-16

Revision Date: 09/01/09
Revised By: J. Raskett

	Issue Date: 7/18/11 Implementation Date: 7/18/11	**Micro-Methods Laboratory** **Log-In Checklist**	DCN: F207 Date Revised: 7-18-11 Revision: 4

Client Chemours **WO** 1603193 **Shipped By** MF
Date/Time Received 3/03/16 @ 1250 **Unpacked/Checked By** MF/ST

Cooler ID	Ice Present Yes/No	Temperature	Thermometer ID	Custody Sealed Yes/No	Custody Seal Intact Yes/No
Client	yes	0.0°c	T#3	no	n/a

If not iced, were samples received within one hour of collection? Yes ___ No ___ [✓ N/A]
Temperature Blank Used Yes ___ [✓ No] If not, temperature taken from cooler ___ or [✓ bottle]
Multi Cooler shipment: ID of samples in coolers that exceed 6°C ___

Custody Seals on Bottles Present Yes ___ [✓ No]
Containers Intact [✓ Yes] No ___
Proper Containers for Requested Analysis [✓ Yes] No ___

Correct Preservation Used for All Samples [✓ Yes] No ___
Adequate Sample for Analysis Requested [✓ Yes] No ___

Volatile Vials Headspace Greater than 6mm in Diameter Yes ___ No ___ [✓ N/A]

Chain of Custody Form Included [✓ Yes] No ___
Chain of Custody Form Complete [✓ Yes] No ___
Chain of Custody Form Properly Relinquished [✓ Yes] No ___
Field Sheets/Special Instructions Included Yes ___ No ___ [✓ N/A]
Samples Missing on COC or From Cooler Yes ___ [✓ No]
Sample Container Labels Match COC [✓ Yes] No ___

Samples Received Within Holding Time [✓ Yes] No ___
Dept. Manager Notified of Rush/Short Holding Times Yes ___ No ___ [✓ N/A]

Does work order meet Micro Methods sample acceptance criteria [✓ Yes] No ___
Note: Samples that do not meet acceptance criteria must be documented in the Sample Rejection Log.

Client Contacted ___ **Contacted By** ___ **Date/Time** ___
Client Instructions: Cancel Work Order ___
Proceed with Work Order ___ **(Data will be qualified)**
Comments: ___

APPENDIX 6-2
ANALYTICAL REPORT FOR IRON CHLORIDE QUARTERLY VOLATILE ORGANIC COMPOUND GRAB SAMPLE

MICRO-METHODS
LABORATORY, INC.

Mailing Address:
PO Box 1410
Ocean Springs, MS
39566-1410

6500 Sunplex Drive
Ocean Springs, MS 39564
228.875.6420 Phone
228.875.6423 Fax

January 13, 2016

Brian Beale

Work Order # : 1601155

The Chemours Company FC LLC
974 Centre Rd.
Wilmington, DE 19805

Purchase Order #: 9900007395

RE: Deepwell TOV

Enclosed are Micro-Methods Laboratory, Inc. results of analyses performed on samples received 01/11/16 15:57. If you have any questions concerning this report, please feel free to contact the office.

Sincerely,

Harry P. Howell

Harry P. Howell

President
Micro-Methods Laboratory, Inc.

ANALYTICAL REPORT FOR SAMPLES

Sample ID	Laboratory ID	Matrix	Date/Time Sampled	Sampled by	Date/Time Received
Deepwell TOV	1601155-01	Liquid	01/10/16 19:30	*Perry Schmidt*	01/11/16 15:57

Sample Receipt Conditions

Date/Time Received: 1/11/2016 3:57:00PM

Shipped by: Lab Pick-up

Received by: Sarah E. Tomek

Submitted by: Tyler C. Dupree

Date/Time Logged: 1/12/2016 7:55:00AM

Logged by: Sarah E. Tomek

Cooler ID: #422

Receipt Temperature: 3.5 °C

Custody Seals	*No*	*Received on Ice*	*Yes*
Containers Intact	*Yes*	*No Ice, Short Trip*	*No*
COC/Labels Agree	*Yes*	*Obvious Contamination*	*No*
Labels Complete	*No*	*Rush to meet HT*	*No*
COC Complete	*Yes*		

The Chemours Company FC LLC 974 Centre Rd. Wilmington DE, 19805	Project: Deepwell TOV Project Number: [none] Project Manager: Brian Beale	**Reported:** 01/13/16 15:40

CASE NARRATIVE SUMMARY

All reported results are within Micro-Methods Laboratory, Inc.defined laboratory quality control objectives unless detailed in narrative summary or identified as qualifications. NOTE: All results listed on this report are calculated on a wet weight basis (as received by the laboratory) unless otherwise noted in the analysis qualification sections.

Summary Comments:

Volatile vials checked at receiving for air bubbles. No visible air bubbles greater than 6mm found.- SET

Volatile technician comments-BSF:
Sample(s) analyzed with zero headspace. 8260B-5030B
pH of sample(s) is less than two in preserved vials. 8260B-5030B

Volatile Organic Compounds-EPA 8260B

Qualifiers:

CC-01 CCV above acceptance limits. Results reported from this calibration were below the reporting limits.

Acetone, Acrolein, Chloromethane, Dichlorodifluoromethane, Vinyl acetate
1601155-01[Deepwell TOV], 6A12005-BLK1

CC-02 ICV exceeds the acceptance limit. Results reported from calibration were below the reporting limits.

Vinyl acetate
1601155-01[Deepwell TOV], 6A12005-BLK1

CC-03 CCV above acceptance limits. QC Results reported from this calibration within acceptance limits.

Acetone, Acrolein, Chloromethane, Dichlorodifluoromethane
6A12005-BS1, 6A12005-BSD1, 6A12005-MS1, 6A12005-MSD1

CC-04 CCV above acceptance limits. Results reported are estimated values.

Acrolein, Vinyl acetate
6A12005-BS1, 6A12005-BSD1, 6A12005-MS1, 6A12005-MSD1

CC-08 ICV above acceptance limits. Results reported are estimated values.

Vinyl acetate
6A12005-BS1, 6A12005-BSD1, 6A12005-MS1, 6A12005-MSD1

L1 LCS and/or LCSD Recovery Limit exceeded.

Acrolein, Vinyl acetate
6A12005-BS1, 6A12005-BSD1

M1 MS/MSD Recovery limit exceeded.

Vinyl acetate
6A12005-MS1, 6A12005-MSD1

The Chemours Company FC LLC
974 Centre Rd.
Wilmington DE, 19805

Project: Deepwell TOV
Project Number: [none]
Project Manager: Brian Beale

Reported:
01/13/16 15:40

Deepwell TOV

1601155-01 (Liquid)

Volatile Organic Compounds by EPA Method 8260B

Analyte	Result	MRL	Units	Dil	Batch	Analyst	Date Time Prepared	Date Time Analyzed	Method	Qualifiers
1,1,1,2-Tetrachloroethane	ND	0.050	mg/kg	1	6A12005	BSF	01/12/16 08:00	01/12/16 17:33	EPA 8260B	
1,1,1-Trichloroethane	ND	0.050	"	"	"	BSF	"	"	"	
1,1,2,2-Tetrachloroethane	ND	0.050	"	"	"	BSF	"	"	"	
1,1,2-Trichloroethane	ND	0.050	"	"	"	BSF	"	"	"	
1,1-Dichloroethane	ND	0.050	"	"	"	BSF	"	"	"	
1,1-Dichloroethene	ND	0.050	"	"	"	BSF	"	"	"	
1,1-Dichloropropene	ND	0.050	"	"	"	BSF	"	"	"	
1,2,3-Trichlorobenzene	ND	0.050	"	"	"	BSF	"	"	"	
1,2,3-Trichloropropane	ND	0.050	"	"	"	BSF	"	"	"	
1,2,4- Trimethylbenzene	ND	0.050	"	"	"	BSF	"	"	"	
1,2,4-Trichlorobenzene	ND	0.050	"	"	"	BSF	"	"	"	
1,2-Dibromo-3-chloropropane	ND	0.050	"	"	"	BSF	"	"	"	
1,2-Dibromoethane (EDB)	ND	0.050	"	"	"	BSF	"	"	"	
1,2-Dichlorobenzene	ND	0.050	"	"	"	BSF	"	"	"	
1,2-Dichloroethane	ND	0.050	"	"	"	BSF	"	"	"	
1,2-Dichloropropane	ND	0.050	"	"	"	BSF	"	"	"	
1,3,5-Trimethylbenzene	ND	0.050	"	"	"	BSF	"	"	"	
1,3-Dichlorobenzene	ND	0.050	"	"	"	BSF	"	"	"	
1,3-Dichloropropane	ND	0.050	"	"	"	BSF	"	"	"	
1,4-Dichlorobenzene	ND	0.050	"	"	"	BSF	"	"	"	
2,2-Dichloropropane	ND	0.050	"	"	"	BSF	"	"	"	
2-Butanone	ND	0.050	"	"	"	BSF	"	"	"	
2-Chlorotoluene	ND	0.050	"	"	"	BSF	"	"	"	
2-Hexanone	ND	0.100	"	"	"	BSF	"	"	"	
4-Chlorotoluene	ND	0.050	"	"	"	BSF	"	"	"	
4-Isopropyltoluene	ND	0.050	"	"	"	BSF	"	"	"	
4-Methyl-2-pentanone	ND	0.100	"	"	"	BSF	"	"	"	
Acetone	ND	0.100	"	"	"	BSF	"	"	"	CC-01
Acrolein	ND	0.050	"	"	"	BSF	"	"	"	CC-01
Acrylonitrile	ND	0.050	"	"	"	BSF	"	"	"	
Benzene	ND	0.050	"	"	"	BSF	"	"	"	
Bromobenzene	ND	0.050	"	"	"	BSF	"	"	"	
Bromochloromethane	ND	0.050	"	"	"	BSF	"	"	"	
Bromodichloromethane	ND	0.050	"	"	"	BSF	"	"	"	
Bromoform	ND	0.050	"	"	"	BSF	"	"	"	
Bromomethane	ND	0.050	"	"	"	BSF	"	"	"	
Carbon disulfide	ND	0.050	"	"	"	BSF	"	"	"	
Carbon Tetrachloride	ND	0.050	"	"	"	BSF	"	"	"	
Chlorobenzene	ND	0.050	"	"	"	BSF	"	"	"	

Deepwell TOV

1601155-01 (Liquid)

Analyte	Result	MRL	Units	Dil	Batch	Analyst	Date Time Prepared	Date Time Analyzed	Method	Qualifiers
Volatile Organic Compounds by EPA Method 8260B										
Chloroethane	ND	0.050	mg/kg	1	6A12005	BSF	01/12/16 08:00	"	"	
Chloroform	ND	0.050	"	"	"	BSF	"	"	"	
Chloromethane	ND	0.050	"	"	"	BSF	"	"	"	CC-01
cis-1,2-Dichloroethene	ND	0.050	"	"	"	BSF	"	"	"	
cis-1,3-Dichloropropene	ND	0.050	"	"	"	BSF	"	"	"	
Dibromochloromethane	ND	0.050	"	"	"	BSF	"	"	"	
Dibromomethane	ND	0.050	"	"	"	BSF	"	"	"	
Dichlorodifluoromethane	ND	0.050	"	"	"	BSF	"	"	"	CC-01
Diethyl ether	ND	0.050	"	"	"	BSF	"	"	"	
Ethylbenzene	ND	0.050	"	"	"	BSF	"	"	"	
Hexachlorobutadiene	ND	0.050	"	"	"	BSF	"	"	"	
Hexane	ND	0.050	"	"	"	BSF	"	"	"	
Iodomethane	ND	0.100	"	"	"	BSF	"	"	"	
Isopropylbenzene	ND	0.050	"	"	"	BSF	"	"	"	
m,p-Xylene	ND	0.050	"	"	"	BSF	"	"	"	
Methyl tert-Butyl Ether	ND	0.050	"	"	"	BSF	"	"	"	
Methylene chloride	ND	0.050	"	"	"	BSF	"	"	"	
Naphthalene	ND	0.100	"	"	"	BSF	"	"	"	
n-Butylbenzene	ND	0.050	"	"	"	BSF	"	"	"	
n-Propyl Benzene	ND	0.050	"	"	"	BSF	"	"	"	
o-Xylene	ND	0.050	"	"	"	BSF	"	"	"	
sec-Butyl Benzene	ND	0.050	"	"	"	BSF	"	"	"	
Styrene	ND	0.050	"	"	"	BSF	"	"	"	
t-Butyl Benzene	ND	0.050	"	"	"	BSF	"	"	"	
Tetrachloroethene	ND	0.050	"	"	"	BSF	"	"	"	
Tetrahydrofuran	ND	0.050	"	"	"	BSF	"	"	"	
Toluene	ND	0.050	"	"	"	BSF	"	"	"	
trans-1,2-Dichloroethene	ND	0.050	"	"	"	BSF	"	"	"	
trans-1,3-Dichloropropene	ND	0.050	"	"	"	BSF	"	"	"	
trans-1,4-Dichloro-2-butene	ND	0.050	"	"	"	BSF	"	"	"	
Trichloroethene	ND	0.050	"	"	"	BSF	"	"	"	
Trichlorofluoromethane	ND	0.050	"	"	"	BSF	"	"	"	
Vinyl acetate	ND	0.050	"	"	"	BSF	"	"	"	CC-01, CC-02
Vinyl chloride	ND	0.050	"	"	"	BSF	"	"	"	

Surrogate		*% Rec*	*Rec Limits*	*Batch*		*Date Time Prepared*	*Date Time Analyzed*	*Method*	*Notes*
Dibromofluoromethane	53.4	*107 %*	*70-130*	"	BSF	"	"	"	
1,2-Dichloroethane-d4	52.7	*105 %*	*70-130*	"	BSF	"	"	"	
Toluene-d8	48.6	*97.2 %*	*70-130*	"	BSF	"	"	"	
4-Bromofluorobenzene	47.9	*95.8 %*	*70-130*	"	BSF	"	"	"	

Volatile Organic Compounds by EPA Method 8260B - Quality Control

Batch 6A12005 - EPA 5030B

Blank (6A12005-BLK1) *Prepared & Analyzed: 01/12/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
1,1,1,2-Tetrachloroethane	ND	0.050	mg/kg							
1,1,1-Trichloroethane	ND	0.050	"							
1,1,2,2-Tetrachloroethane	ND	0.050	"							
1,1,2-Trichloroethane	ND	0.050	"							
1,1,2-Trichlorotrifluoroethane	ND	0.050	"							
1,1-Dichloroethane	ND	0.050	"							
1,1-Dichloroethene	ND	0.050	"							
1,1-Dichloropropene	ND	0.050	"							
1,2,3-Trichlorobenzene	ND	0.050	"							
1,2,3-Trichloropropane	ND	0.050	"							
1,2,4- Trimethylbenzene	ND	0.050	"							
1,2,4-Trichlorobenzene	ND	0.050	"							
1,2-Dibromo-3-chloropropane	ND	0.050	"							
1,2-Dibromoethane (EDB)	ND	0.050	"							
1,2-Dichlorobenzene	ND	0.050	"							
1,2-Dichloroethane	ND	0.050	"							
1,2-Dichloropropane	ND	0.050	"							
1,3,5-Trimethylbenzene	ND	0.050	"							
1,3-Dichlorobenzene	ND	0.050	"							
1,3-Dichloropropane	ND	0.050	"							
1,4-Dichlorobenzene	ND	0.050	"							
1,4-Dioxane	ND	0.500	"							
2,2-Dichloropropane	ND	0.050	"							
2-Butanone	ND	0.050	"							
2-Chloroethylvinyl ether	ND	0.050	"							
2-Chlorotoluene	ND	0.050	"							
2-Hexanone	ND	0.100	"							
4-Chlorotoluene	ND	0.050	"							
4-Isopropyltoluene	ND	0.050	"							
4-Methyl-2-pentanone	ND	0.100	"							
Acetone	ND	0.100	"							CC-01
Acrolein	ND	0.050	"							CC-01
Acrylonitrile	ND	0.050	"							
Benzene	ND	0.050	"							
Bromobenzene	ND	0.050	"							
Bromochloromethane	ND	0.050	"							
Bromodichloromethane	ND	0.050	"							
Bromoform	ND	0.050	"							
Bromomethane	ND	0.050	"							
Carbon disulfide	ND	0.050	"							
Carbon Tetrachloride	ND	0.050	"							
Chlorobenzene	ND	0.050	"							
Chloroethane	ND	0.050	"							
Chloroform	ND	0.050	"							
Chloromethane	ND	0.050	"							CC-01

Volatile Organic Compounds by EPA Method 8260B - Quality Control

Batch 6A12005 - EPA 5030B

Blank (6A12005-BLK1) ***Prepared & Analyzed: 01/12/16***

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
cis-1,2-Dichloroethene	ND	0.050	mg/kg							
cis-1,3-Dichloropropene	ND	0.050	"							
cis-1,4-Dichloro-2-butene	ND	0.050	"							
Dibromochloromethane	ND	0.050	"							
Dibromomethane	ND	0.050	"							
Dichlorodifluoromethane	ND	0.050	"							CC-01
Diethyl ether	ND	0.050	"							
Ethylbenzene	ND	0.050	"							
Hexachlorobutadiene	ND	0.050	"							
Hexane	ND	0.050	"							
Iodomethane	ND	0.100	"							
Isobutanol	ND	0.200	"							
Isopropylbenzene	ND	0.050	"							
m,p-Xylene	ND	0.050	"							
Methyl Acrylate	ND	0.050	"							
Methyl tert-Butyl Ether	ND	0.050	"							
Methylene chloride	ND	0.050	"							
Naphthalene	ND	0.100	"							
n-Butylbenzene	ND	0.050	"							
n-Propyl Benzene	ND	0.050	"							
o-Xylene	ND	0.050	"							
sec-Butyl Benzene	ND	0.050	"							
Styrene	ND	0.050	"							
t-Butyl Benzene	ND	0.050	"							
Tert-butyl alcohol	ND	0.500	"							
Tetrachloroethene	ND	0.050	"							
Tetrahydrofuran	ND	0.050	"							
Toluene	ND	0.050	"							
trans-1,2-Dichloroethene	ND	0.050	"							
trans-1,3-Dichloropropene	ND	0.050	"							
trans-1,4-Dichloro-2-butene	ND	0.050	"							
Trichloroethene	ND	0.050	"							
Trichlorofluoromethane	ND	0.050	"							
Vinyl acetate	ND	0.050	"							CC-01, CC-02
Vinyl chloride	ND	0.050	"							
Surrogate: Dibromofluoromethane	*0.0522*		*"*	*0.0500*		*104*	*70-130*			
Surrogate: 1,2-Dichloroethane-d4	*0.0498*		*"*	*0.0500*		*99.6*	*70-130*			
Surrogate: Toluene-d8	*0.0487*		*"*	*0.0500*		*97.4*	*70-130*			
Surrogate: 4-Bromofluorobenzene	*0.0471*		*"*	*0.0500*		*94.1*	*70-130*			

Volatile Organic Compounds by EPA Method 8260B - Quality Control

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Batch 6A12005 - EPA 5030B										
LCS (6A12005-BS1)						***Prepared & Analyzed: 01/12/16***				
1,1,1,2-Tetrachloroethane	0.020	0.050	mg/kg	0.0200		97.7	70-130			
1,1,1-Trichloroethane	0.021	0.050	"	0.0200		104	70-130			
1,1,2,2-Tetrachloroethane	0.019	0.050	"	0.0200		94.2	70-130			
1,1,2-Trichloroethane	0.020	0.050	"	0.0200		101	70-130			
1,1-Dichloroethane	0.021	0.050	"	0.0200		103	74.6-139			
1,1-Dichloroethene	0.019	0.050	"	0.0200		96.6	72.8-138			
1,1-Dichloropropene	0.020	0.050	"	0.0200		100	70-130			
1,2,3-Trichlorobenzene	0.020	0.050	"	0.0200		97.7	66.1-122			
1,2,3-Trichloropropane	0.020	0.050	"	0.0200		101	70-130			
1,2,4- Trimethylbenzene	0.020	0.050	"	0.0200		99.3	70-130			
1,2,4-Trichlorobenzene	0.018	0.050	"	0.0200		92.2	70-130			
1,2-Dibromo-3-chloropropane	0.018	0.050	"	0.0200		91.7	70-130			
1,2-Dibromoethane (EDB)	0.021	0.050	"	0.0200		105	70-130			
1,2-Dichlorobenzene	0.019	0.050	"	0.0200		94.7	70-130			
1,2-Dichloroethane	0.022	0.050	"	0.0200		110	70-130			
1,2-Dichloropropane	0.020	0.050	"	0.0200		99.4	70-130			
1,3,5-Trimethylbenzene	0.020	0.050	"	0.0200		101	70-130			
1,3-Dichlorobenzene	0.020	0.050	"	0.0200		97.8	70-130			
1,3-Dichloropropane	0.021	0.050	"	0.0200		106	70-130			
1,4-Dichlorobenzene	0.018	0.050	"	0.0200		92.1	70-130			
1,4-Dioxane	ND	0.500	"	0.0200			5-215			
2,2-Dichloropropane	0.020	0.050	"	0.0200		99.8	70-130			
2-Butanone	0.019	0.050	"	0.0200		96.7	58.5-136			
2-Chloroethylvinyl ether	ND	0.050	"	0.0200			62.9-139			
2-Chlorotoluene	0.020	0.050	"	0.0200		98.4	70-130			
2-Hexanone	0.018	0.100	"	0.0200		87.9	55.1-136			
4-Chlorotoluene	0.019	0.050	"	0.0200		96.3	70-130			
4-Isopropyltoluene	0.019	0.050	"	0.0200		93.6	70-130			
4-Methyl-2-pentanone	0.019	0.100	"	0.0200		94.9	50.2-131			
Acetone	0.023	0.100	"	0.0200		113	27.7-177			CC-03
Acrolein	0.030	0.050	"	0.0200		149	48.9-143			CC-04, L1
Acrylonitrile	0.022	0.050	"	0.0200		112	58.1-142			
Benzene	0.019	0.050	"	0.0200		95.1	70-130			
Bromobenzene	0.020	0.050	"	0.0200		99.4	70-130			
Bromochloromethane	0.021	0.050	"	0.0200		105	70-130			
Bromodichloromethane	0.021	0.050	"	0.0200		106	70-130			
Bromoform	0.019	0.050	"	0.0200		95.7	70-130			
Bromomethane	0.019	0.050	"	0.0200		95.9	58.1-148			
Carbon disulfide	0.019	0.050	"	0.0200		96.4	65.3-138			
Carbon Tetrachloride	0.021	0.050	"	0.0200		105	70-130			
Chlorobenzene	0.019	0.050	"	0.0200		94.6	70-130			
Chloroethane	0.019	0.050	"	0.0200		94.3	53.6-151			
Chloroform	0.020	0.050	"	0.0200		101	70-130			
Chloromethane	0.015	0.050	"	0.0200		75.4	58.8-115			CC-03
cis-1,2-Dichloroethene	0.020	0.050	"	0.0200		98.8	70-130			

Volatile Organic Compounds by EPA Method 8260B - Quality Control

Batch 6A12005 - EPA 5030B

LCS (6A12005-BS1) *Prepared & Analyzed: 01/12/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
cis-1,3-Dichloropropene	0.020	0.050	mg/kg	0.0200		99.0	70-130			
Dibromochloromethane	0.020	0.050	"	0.0200		101	70-130			
Dibromomethane	0.021	0.050	"	0.0200		107	70-130			
Dichlorodifluoromethane	0.014	0.050	"	0.0200		67.5	36.8-126			CC-03
Diethyl ether	0.021	0.050	"	0.0200		104	70-130			
Ethylbenzene	0.019	0.050	"	0.0200		94.6	70-130			
Hexachlorobutadiene	0.020	0.050	"	0.0200		101	70-130			
Hexane	0.020	0.050	"	0.0200		98.3	70-130			
Iodomethane	0.020	0.100	"	0.0200		100	64.6-131			
Isobutanol	ND	0.200	"	0.0200			5-158			
Isopropylbenzene	0.020	0.050	"	0.0200		97.8	70-130			
m,p-Xylene	0.040	0.050	"	0.0400		98.8	70-130			
Methyl Acrylate	0.018	0.050	"	0.0200		91.7	70-130			
Methyl tert-Butyl Ether	0.020	0.050	"	0.0200		100	70-130			
Methylene chloride	0.020	0.050	"	0.0200		99.4	71.6-142			
Naphthalene	0.019	0.100	"	0.0200		95.7	56.4-133			
n-Butylbenzene	0.018	0.050	"	0.0200		91.9	70-130			
n-Propyl Benzene	0.019	0.050	"	0.0200		97.3	70-130			
o-Xylene	0.020	0.050	"	0.0200		99.2	70-130			
sec-Butyl Benzene	0.019	0.050	"	0.0200		97.4	70-130			
Styrene	0.019	0.050	"	0.0200		96.6	70-130			
t-Butyl Benzene	0.020	0.050	"	0.0200		100	70-130			
Tetrachloroethene	0.021	0.050	"	0.0200		103	70-130			
Tetrahydrofuran	0.019	0.050	"	0.0200		94.6	50.8-141			
Toluene	0.020	0.050	"	0.0200		99.5	70-130			
trans-1,2-Dichloroethene	0.020	0.050	"	0.0200		99.7	73.6-138			
trans-1,3-Dichloropropene	0.021	0.050	"	0.0200		103	70-130			
trans-1,4-Dichloro-2-butene	0.018	0.050	"	0.0200		91.6	59.2-145			
Trichloroethene	0.020	0.050	"	0.0200		100	70-130			
Trichlorofluoromethane	0.020	0.050	"	0.0200		98.1	71.7-149			
Vinyl acetate	0.028	0.050	"	0.0200		142	66.6-129			CC-04, CC-08, L1
Vinyl chloride	0.018	0.050	"	0.0200		88.6	70-130			
Surrogate: Dibromofluoromethane	*0.0527*		*"*	*0.0500*		*105*	*70-130*			
Surrogate: 1,2-Dichloroethane-d4	*0.0522*		*"*	*0.0500*		*104*	*70-130*			
Surrogate: Toluene-d8	*0.0484*		*"*	*0.0500*		*96.7*	*70-130*			
Surrogate: 4-Bromofluorobenzene	*0.0505*		*"*	*0.0500*		*101*	*70-130*			

Volatile Organic Compounds by EPA Method 8260B - Quality Control

Batch 6A12005 - EPA 5030B

LCS Dup (6A12005-BSD1) *Prepared & Analyzed: 01/12/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
1,1,1,2-Tetrachloroethane	0.020	0.050	mg/kg	0.0200		101	70-130	3.52	35	
1,1,1-Trichloroethane	0.022	0.050	"	0.0200		108	70-130	4.05	35	
1,1,2,2-Tetrachloroethane	0.019	0.050	"	0.0200		95.9	70-130	1.84	35	
1,1,2-Trichloroethane	0.021	0.050	"	0.0200		103	70-130	2.65	35	
1,1-Dichloroethane	0.021	0.050	"	0.0200		106	74.6-139	3.02	35	
1,1-Dichloroethene	0.021	0.050	"	0.0200		106	72.8-138	9.33	35	
1,1-Dichloropropene	0.021	0.050	"	0.0200		106	70-130	5.69	35	
1,2,3-Trichlorobenzene	0.020	0.050	"	0.0200		102	66.1-122	4.55	35	
1,2,3-Trichloropropane	0.020	0.050	"	0.0200		99.7	70-130	1.34	35	
1,2,4- Trimethylbenzene	0.020	0.050	"	0.0200		102	70-130	2.68	35	
1,2,4-Trichlorobenzene	0.019	0.050	"	0.0200		95.9	70-130	3.93	35	
1,2-Dibromo-3-chloropropane	0.018	0.050	"	0.0200		88.6	70-130	3.44	35	
1,2-Dibromoethane (EDB)	0.021	0.050	"	0.0200		106	70-130	0.995	35	
1,2-Dichlorobenzene	0.019	0.050	"	0.0200		95.3	70-130	0.684	35	
1,2-Dichloroethane	0.022	0.050	"	0.0200		110	70-130	0.0907	35	
1,2-Dichloropropane	0.020	0.050	"	0.0200		102	70-130	2.78	35	
1,3,5-Trimethylbenzene	0.021	0.050	"	0.0200		104	70-130	3.13	35	
1,3-Dichlorobenzene	0.020	0.050	"	0.0200		101	70-130	2.77	35	
1,3-Dichloropropane	0.021	0.050	"	0.0200		104	70-130	1.71	35	
1,4-Dichlorobenzene	0.019	0.050	"	0.0200		96.4	70-130	4.56	35	
1,4-Dioxane	ND	0.500	"	0.0200			5-215		35	
2,2-Dichloropropane	0.021	0.050	"	0.0200		103	70-130	3.40	35	
2-Butanone	0.020	0.050	"	0.0200		97.9	58.5-136	1.18	35	
2-Chloroethylvinyl ether	ND	0.050	"	0.0200			62.9-139		35	
2-Chlorotoluene	0.020	0.050	"	0.0200		99.6	70-130	1.26	35	
2-Hexanone	0.019	0.100	"	0.0200		92.7	55.1-136	5.26	35	
4-Chlorotoluene	0.020	0.050	"	0.0200		100	70-130	4.22	35	
4-Isopropyltoluene	0.019	0.050	"	0.0200		97.1	70-130	3.72	35	
4-Methyl-2-pentanone	0.020	0.100	"	0.0200		99.1	50.2-131	4.33	35	
Acetone	0.021	0.100	"	0.0200		105	27.7-177	7.61	35	CC-03
Acrolein	0.028	0.050	"	0.0200		138	48.9-143	8.05	35	CC-03
Acrylonitrile	0.023	0.050	"	0.0200		116	58.1-142	3.25	35	
Benzene	0.020	0.050	"	0.0200		101	70-130	5.82	35	
Bromobenzene	0.020	0.050	"	0.0200		99.1	70-130	0.302	35	
Bromochloromethane	0.022	0.050	"	0.0200		108	70-130	2.76	35	
Bromodichloromethane	0.021	0.050	"	0.0200		106	70-130	0.424	35	
Bromoform	0.020	0.050	"	0.0200		101	70-130	5.19	35	
Bromomethane	0.021	0.050	"	0.0200		103	58.1-148	6.75	35	
Carbon disulfide	0.021	0.050	"	0.0200		103	65.3-138	6.91	35	
Carbon Tetrachloride	0.023	0.050	"	0.0200		115	70-130	8.32	35	
Chlorobenzene	0.019	0.050	"	0.0200		96.9	70-130	2.40	35	
Chloroethane	0.020	0.050	"	0.0200		99.8	53.6-151	5.67	35	
Chloroform	0.021	0.050	"	0.0200		105	70-130	3.59	35	
Chloromethane	0.016	0.050	"	0.0200		82.0	58.8-115	8.45	35	CC-03
cis-1,2-Dichloroethene	0.020	0.050	"	0.0200		99.6	70-130	0.756	35	

Volatile Organic Compounds by EPA Method 8260B - Quality Control

Batch 6A12005 - EPA 5030B

LCS Dup (6A12005-BSD1) *Prepared & Analyzed: 01/12/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
cis-1,3-Dichloropropene	0.020	0.050	mg/kg	0.0200		99.7	70-130	0.755	35	
Dibromochloromethane	0.021	0.050	"	0.0200		105	70-130	3.89	35	
Dibromomethane	0.022	0.050	"	0.0200		108	70-130	0.980	35	
Dichlorodifluoromethane	0.012	0.050	"	0.0200		60.8	36.8-126	10.5	35	CC-03
Diethyl ether	0.022	0.050	"	0.0200		108	70-130	4.15	35	
Ethylbenzene	0.020	0.050	"	0.0200		98.4	70-130	3.99	35	
Hexachlorobutadiene	0.020	0.050	"	0.0200		102	70-130	1.73	35	
Hexane	0.021	0.050	"	0.0200		103	70-130	4.62	35	
Iodomethane	0.022	0.100	"	0.0200		109	64.6-131	7.95	35	
Isobutanol	ND	0.200	"	0.0200			5-158		35	
Isopropylbenzene	0.020	0.050	"	0.0200		102	70-130	4.16	35	
m,p-Xylene	0.041	0.050	"	0.0400		102	70-130	3.12	35	
Methyl Acrylate	0.019	0.050	"	0.0200		95.5	70-130	4.06	35	
Methyl tert-Butyl Ether	0.021	0.050	"	0.0200		104	70-130	4.25	35	
Methylene chloride	0.021	0.050	"	0.0200		105	71.6-142	5.76	35	
Naphthalene	0.020	0.100	"	0.0200		98.0	56.4-133	2.38	35	
n-Butylbenzene	0.019	0.050	"	0.0200		95.8	70-130	4.10	35	
n-Propyl Benzene	0.020	0.050	"	0.0200		101	70-130	3.68	35	
o-Xylene	0.020	0.050	"	0.0200		102	70-130	2.83	35	
sec-Butyl Benzene	0.020	0.050	"	0.0200		102	70-130	4.37	35	
Styrene	0.020	0.050	"	0.0200		101	70-130	4.65	35	
t-Butyl Benzene	0.021	0.050	"	0.0200		104	70-130	3.73	35	
Tetrachloroethene	0.021	0.050	"	0.0200		107	70-130	4.15	35	
Tetrahydrofuran	0.020	0.050	"	0.0200		100	50.8-141	5.85	35	
Toluene	0.020	0.050	"	0.0200		101	70-130	1.45	35	
trans-1,2-Dichloroethene	0.021	0.050	"	0.0200		106	73.6-138	6.22	35	
trans-1,3-Dichloropropene	0.021	0.050	"	0.0200		106	70-130	2.67	35	
trans-1,4-Dichloro-2-butene	0.019	0.050	"	0.0200		95.0	59.2-145	3.64	35	
Trichloroethene	0.021	0.050	"	0.0200		105	70-130	4.15	35	
Trichlorofluoromethane	0.020	0.050	"	0.0200		101	71.7-149	2.42	35	
Vinyl acetate	0.027	0.050	"	0.0200		135	66.6-129	5.60	35	CC-04, CC-08, L1
Vinyl chloride	0.020	0.050	"	0.0200		97.6	70-130	9.72	35	
Surrogate: Dibromofluoromethane	*0.0533*		*"*	*0.0500*		*107*	*70-130*			
Surrogate: 1,2-Dichloroethane-d4	*0.0518*		*"*	*0.0500*		*104*	*70-130*			
Surrogate: Toluene-d8	*0.0486*		*"*	*0.0500*		*97.2*	*70-130*			
Surrogate: 4-Bromofluorobenzene	*0.0506*		*"*	*0.0500*		*101*	*70-130*			

Volatile Organic Compounds by EPA Method 8260B - Quality Control

Batch 6A12005 - EPA 5030B

Matrix Spike (6A12005-MS1) **Source: 1601149-01** ***Prepared & Analyzed: 01/12/16***

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
1,1,1,2-Tetrachloroethane	0.020	0.050	mg/kg	0.0200	ND	99.7	70-130			
1,1,1-Trichloroethane	0.022	0.050	"	0.0200	ND	110	70-130			
1,1,2,2-Tetrachloroethane	0.019	0.050	"	0.0200	ND	93.2	71.9-140			
1,1,2-Trichloroethane	0.021	0.050	"	0.0200	ND	103	70-130			
1,1-Dichloroethane	0.021	0.050	"	0.0200	ND	105	78.8-143			
1,1-Dichloroethene	0.020	0.050	"	0.0200	ND	102	72.8-143			
1,1-Dichloropropene	0.021	0.050	"	0.0200	ND	105	70-130			
1,2,3-Trichlorobenzene	0.019	0.050	"	0.0200	ND	94.6	53.4-121			
1,2,3-Trichloropropane	0.019	0.050	"	0.0200	ND	97.3	70-130			
1,2,4- Trimethylbenzene	0.019	0.050	"	0.0200	ND	97.3	41.2-145			
1,2,4-Trichlorobenzene	0.018	0.050	"	0.0200	ND	87.9	53.6-116			
1,2-Dibromo-3-chloropropane	0.018	0.050	"	0.0200	ND	89.8	59-129			
1,2-Dibromoethane (EDB)	0.021	0.050	"	0.0200	ND	105	70-130			
1,2-Dichlorobenzene	0.018	0.050	"	0.0200	ND	92.0	70-130			
1,2-Dichloroethane	0.022	0.050	"	0.0200	ND	110	70-130			
1,2-Dichloropropane	0.020	0.050	"	0.0200	ND	99.4	70-130			
1,3,5-Trimethylbenzene	0.019	0.050	"	0.0200	ND	96.8	48.3-143			
1,3-Dichlorobenzene	0.020	0.050	"	0.0200	ND	100	70-130			
1,3-Dichloropropane	0.021	0.050	"	0.0200	ND	103	70-130			
1,4-Dichlorobenzene	0.019	0.050	"	0.0200	ND	93.2	70-130			
1,4-Dioxane	ND	0.500	"	0.0200	ND		0-0			
2,2-Dichloropropane	0.020	0.050	"	0.0200	ND	97.8	58.6-138			
2-Butanone	0.019	0.050	"	0.0200	ND	96.0	56.9-131			
2-Chloroethylvinyl ether	ND	0.050	"	0.0200	ND		33.3-180			
2-Chlorotoluene	0.019	0.050	"	0.0200	ND	97.3	70-130			
2-Hexanone	0.018	0.100	"	0.0200	ND	89.0	54.7-128			
4-Chlorotoluene	0.019	0.050	"	0.0200	ND	97.4	70-130			
4-Isopropyltoluene	0.019	0.050	"	0.0200	ND	93.3	70-130			
4-Methyl-2-pentanone	0.019	0.100	"	0.0200	ND	95.4	45.7-133			
Acetone	0.023	0.100	"	0.0200	ND	116	48.4-154			CC-03
Acrolein	0.027	0.050	"	0.0200	ND	134	13.4-177			CC-03
Acrylonitrile	0.022	0.050	"	0.0200	ND	111	62.1-135			
Benzene	0.020	0.050	"	0.0200	ND	98.2	70-130			
Bromobenzene	0.019	0.050	"	0.0200	ND	96.8	70-130			
Bromochloromethane	0.021	0.050	"	0.0200	ND	103	70-130			
Bromodichloromethane	0.021	0.050	"	0.0200	ND	106	70-130			
Bromoform	0.017	0.050	"	0.0200	ND	86.9	60.7-127			
Bromomethane	0.019	0.050	"	0.0200	ND	93.6	67.1-144			
Carbon disulfide	0.016	0.050	"	0.0200	ND	78.3	46.2-151			
Carbon Tetrachloride	0.022	0.050	"	0.0200	ND	111	69.8-136			
Chlorobenzene	0.019	0.050	"	0.0200	ND	96.5	70-130			
Chloroethane	0.018	0.050	"	0.0200	ND	91.5	54.8-152			
Chloroform	0.021	0.050	"	0.0200	ND	105	70-130			
Chloromethane	0.016	0.050	"	0.0200	ND	82.4	57.5-121			CC-03
cis-1,2-Dichloroethene	0.020	0.050	"	0.0200	ND	101	70-130			

Volatile Organic Compounds by EPA Method 8260B - Quality Control

Batch 6A12005 - EPA 5030B

Matrix Spike (6A12005-MS1) **Source: 1601149-01** ***Prepared & Analyzed: 01/12/16***

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
cis-1,3-Dichloropropene	0.019	0.050	mg/kg	0.0200	ND	93.3	70-130			
Dibromochloromethane	0.020	0.050	"	0.0200	ND	99.3	67.2-125			
Dibromomethane	0.021	0.050	"	0.0200	ND	105	70-130			
Dichlorodifluoromethane	0.010	0.050	"	0.0200	ND	48.8	38.4-121			CC-03
Diethyl ether	0.021	0.050	"	0.0200	ND	103	76-137			
Ethylbenzene	0.019	0.050	"	0.0200	ND	96.6	70-130			
Hexachlorobutadiene	0.020	0.050	"	0.0200	ND	100	57.2-120			
Hexane	0.020	0.050	"	0.0200	ND	99.9	69.8-135			
Iodomethane	0.022	0.100	"	0.0200	ND	108	56.3-146			
Isobutanol	ND	0.200	"	0.0200	ND		5-147			
Isopropylbenzene	0.019	0.050	"	0.0200	ND	97.4	70-130			
m,p-Xylene	0.040	0.050	"	0.0400	ND	99.3	63.9-131			
Methyl Acrylate	0.019	0.050	"	0.0200	ND	93.3	63.3-126			
Methyl tert-Butyl Ether	0.020	0.050	"	0.0200	ND	99.0	77.3-136			
Methylene chloride	0.021	0.050	"	0.0200	ND	105	74.2-144			
Naphthalene	0.019	0.100	"	0.0200	ND	94.0	25.8-134			
n-Butylbenzene	0.018	0.050	"	0.0200	ND	90.9	67.2-115			
n-Propyl Benzene	0.020	0.050	"	0.0200	ND	97.7	70-130			
o-Xylene	0.019	0.050	"	0.0200	ND	96.0	60.7-129			
sec-Butyl Benzene	0.019	0.050	"	0.0200	ND	97.1	70-130			
Styrene	0.018	0.050	"	0.0200	ND	91.9	10.5-158			
t-Butyl Benzene	0.020	0.050	"	0.0200	ND	101	70-130			
Tetrachloroethene	0.021	0.050	"	0.0200	ND	105	70-130			
Tetrahydrofuran	0.018	0.050	"	0.0200	ND	89.6	35.5-149			
Toluene	0.020	0.050	"	0.0200	ND	101	70-130			
trans-1,2-Dichloroethene	0.021	0.050	"	0.0200	ND	105	71.7-144			
trans-1,3-Dichloropropene	0.020	0.050	"	0.0200	ND	99.8	65-115			
trans-1,4-Dichloro-2-butene	0.016	0.050	"	0.0200	ND	78.1	53.1-150			
Trichloroethene	0.021	0.050	"	0.0200	ND	105	70-130			
Trichlorofluoromethane	0.020	0.050	"	0.0200	ND	102	68.3-161			
Vinyl acetate	0.030	0.050	"	0.0200	ND	152	55-132			CC-04, CC-08, M1
Vinyl chloride	0.018	0.050	"	0.0200	ND	89.3	65-127			
Surrogate: Dibromofluoromethane	*0.0546*		"	*0.0500*		*109*	*70-130*			
Surrogate: 1,2-Dichloroethane-d4	*0.0516*		"	*0.0500*		*103*	*70-130*			
Surrogate: Toluene-d8	*0.0478*		"	*0.0500*		*95.5*	*70-130*			
Surrogate: 4-Bromofluorobenzene	*0.0505*		"	*0.0500*		*101*	*70-130*			

Volatile Organic Compounds by EPA Method 8260B - Quality Control

Batch 6A12005 - EPA 5030B

Matrix Spike Dup (6A12005-MSD1) **Source: 1601149-01** ***Prepared & Analyzed: 01/12/16***

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
1,1,1,2-Tetrachloroethane	0.019	0.050	mg/kg	0.0200	ND	96.1	70-130	3.73	40	
1,1,1-Trichloroethane	0.021	0.050	"	0.0200	ND	106	70-130	4.31	40	
1,1,2,2-Tetrachloroethane	0.019	0.050	"	0.0200	ND	94.7	71.9-140	1.60	40	
1,1,2-Trichloroethane	0.020	0.050	"	0.0200	ND	98.4	70-130	4.67	40	
1,1-Dichloroethane	0.021	0.050	"	0.0200	ND	104	78.8-143	0.573	40	
1,1-Dichloroethene	0.020	0.050	"	0.0200	ND	101	72.8-143	0.838	40	
1,1-Dichloropropene	0.020	0.050	"	0.0200	ND	102	70-130	3.48	40	
1,2,3-Trichlorobenzene	0.019	0.050	"	0.0200	ND	93.1	53.4-121	1.65	40	
1,2,3-Trichloropropane	0.020	0.050	"	0.0200	ND	100	70-130	2.84	40	
1,2,4- Trimethylbenzene	0.019	0.050	"	0.0200	ND	93.4	41.2-145	4.09	40	
1,2,4-Trichlorobenzene	0.017	0.050	"	0.0200	ND	85.6	53.6-116	2.65	40	
1,2-Dibromo-3-chloropropane	0.017	0.050	"	0.0200	ND	86.9	59-129	3.28	40	
1,2-Dibromoethane (EDB)	0.021	0.050	"	0.0200	ND	103	70-130	1.77	40	
1,2-Dichlorobenzene	0.018	0.050	"	0.0200	ND	91.8	70-130	0.163	40	
1,2-Dichloroethane	0.022	0.050	"	0.0200	ND	108	70-130	1.37	40	
1,2-Dichloropropane	0.020	0.050	"	0.0200	ND	99.5	70-130	0.101	40	
1,3,5-Trimethylbenzene	0.019	0.050	"	0.0200	ND	96.4	48.3-143	0.466	40	
1,3-Dichlorobenzene	0.019	0.050	"	0.0200	ND	96.8	70-130	3.45	40	
1,3-Dichloropropane	0.020	0.050	"	0.0200	ND	102	70-130	1.12	40	
1,4-Dichlorobenzene	0.018	0.050	"	0.0200	ND	91.0	70-130	2.44	40	
1,4-Dioxane	ND	0.500	"	0.0200	ND		0-0		40	
2,2-Dichloropropane	0.019	0.050	"	0.0200	ND	93.5	58.6-138	4.50	40	
2-Butanone	0.020	0.050	"	0.0200	ND	98.7	56.9-131	2.83	40	
2-Chloroethylvinyl ether	ND	0.050	"	0.0200	ND		33.3-180		40	
2-Chlorotoluene	0.019	0.050	"	0.0200	ND	96.4	70-130	0.878	40	
2-Hexanone	0.018	0.100	"	0.0200	ND	90.1	54.7-128	1.23	40	
4-Chlorotoluene	0.019	0.050	"	0.0200	ND	95.8	70-130	1.60	40	
4-Isopropyltoluene	0.018	0.050	"	0.0200	ND	90.8	70-130	2.72	40	
4-Methyl-2-pentanone	0.018	0.100	"	0.0200	ND	91.7	45.7-133	3.96	40	
Acetone	0.021	0.100	"	0.0200	ND	106	48.4-154	9.16	40	CC-03
Acrolein	0.028	0.050	"	0.0200	ND	139	13.4-177	4.00	40	CC-03
Acrylonitrile	0.023	0.050	"	0.0200	ND	114	62.1-135	3.20	40	
Benzene	0.019	0.050	"	0.0200	ND	95.4	70-130	2.89	40	
Bromobenzene	0.019	0.050	"	0.0200	ND	97.1	70-130	0.310	40	
Bromochloromethane	0.020	0.050	"	0.0200	ND	102	70-130	1.61	40	
Bromodichloromethane	0.021	0.050	"	0.0200	ND	103	70-130	3.45	40	
Bromoform	0.018	0.050	"	0.0200	ND	92.2	60.7-127	5.98	40	
Bromomethane	0.019	0.050	"	0.0200	ND	94.8	67.1-144	1.33	40	
Carbon disulfide	0.015	0.050	"	0.0200	ND	76.6	46.2-151	2.13	40	
Carbon Tetrachloride	0.022	0.050	"	0.0200	ND	109	69.8-136	1.64	40	
Chlorobenzene	0.019	0.050	"	0.0200	ND	93.7	70-130	2.89	40	
Chloroethane	0.019	0.050	"	0.0200	ND	92.9	54.8-152	1.52	40	
Chloroform	0.021	0.050	"	0.0200	ND	103	70-130	1.97	40	
Chloromethane	0.014	0.050	"	0.0200	ND	72.4	57.5-121	12.9	40	CC-03
cis-1,2-Dichloroethene	0.020	0.050	"	0.0200	ND	100	70-130	0.199	40	

Volatile Organic Compounds by EPA Method 8260B - Quality Control

Batch 6A12005 - EPA 5030B

Matrix Spike Dup (6A12005-MSD1) **Source: 1601149-01** ***Prepared & Analyzed: 01/12/16***

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
cis-1,3-Dichloropropene	0.019	0.050	mg/kg	0.0200	ND	95.4	70-130	2.23	40	
Dibromochloromethane	0.020	0.050	"	0.0200	ND	98.4	67.2-125	0.910	40	
Dibromomethane	0.021	0.050	"	0.0200	ND	106	70-130	1.37	40	
Dichlorodifluoromethane	0.009	0.050	"	0.0200	ND	46.9	38.4-121	3.97	40	CC-03
Diethyl ether	0.021	0.050	"	0.0200	ND	104	76-137	0.916	40	
Ethylbenzene	0.019	0.050	"	0.0200	ND	94.2	70-130	2.57	40	
Hexachlorobutadiene	0.019	0.050	"	0.0200	ND	94.4	57.2-120	5.96	40	
Hexane	0.019	0.050	"	0.0200	ND	94.0	69.8-135	6.14	40	
Iodomethane	0.021	0.100	"	0.0200	ND	106	56.3-146	1.97	40	
Isobutanol	ND	0.200	"	0.0200	ND		5-147		40	
Isopropylbenzene	0.019	0.050	"	0.0200	ND	97.2	70-130	0.206	40	
m,p-Xylene	0.039	0.050	"	0.0400	ND	97.1	63.9-131	2.21	40	
Methyl Acrylate	0.020	0.050	"	0.0200	ND	98.4	63.3-126	5.32	40	
Methyl tert-Butyl Ether	0.020	0.050	"	0.0200	ND	102	77.3-136	2.54	40	
Methylene chloride	0.021	0.050	"	0.0200	ND	103	74.2-144	1.97	40	
Naphthalene	0.019	0.100	"	0.0200	ND	94.9	25.8-134	0.900	40	
n-Butylbenzene	0.017	0.050	"	0.0200	ND	86.5	67.2-115	4.96	40	
n-Propyl Benzene	0.019	0.050	"	0.0200	ND	95.2	70-130	2.59	40	
o-Xylene	0.019	0.050	"	0.0200	ND	97.4	60.7-129	1.40	40	
sec-Butyl Benzene	0.019	0.050	"	0.0200	ND	95.9	70-130	1.19	40	
Styrene	0.018	0.050	"	0.0200	ND	89.3	10.5-158	2.87	40	
t-Butyl Benzene	0.019	0.050	"	0.0200	ND	96.9	70-130	3.90	40	
Tetrachloroethene	0.020	0.050	"	0.0200	ND	101	70-130	3.40	40	
Tetrahydrofuran	0.019	0.050	"	0.0200	ND	94.1	35.5-149	4.90	40	
Toluene	0.020	0.050	"	0.0200	ND	97.8	70-130	2.92	40	
trans-1,2-Dichloroethene	0.020	0.050	"	0.0200	ND	99.8	71.7-144	5.32	40	
trans-1,3-Dichloropropene	0.020	0.050	"	0.0200	ND	99.3	65-115	0.502	40	
trans-1,4-Dichloro-2-butene	0.015	0.050	"	0.0200	ND	75.9	53.1-150	2.92	40	
Trichloroethene	0.020	0.050	"	0.0200	ND	101	70-130	4.28	40	
Trichlorofluoromethane	0.020	0.050	"	0.0200	ND	101	68.3-161	1.04	40	
Vinyl acetate	0.030	0.050	"	0.0200	ND	151	55-132	0.0991	40	CC-04, CC-08, M1
Vinyl chloride	0.018	0.050	"	0.0200	ND	90.8	65-127	1.67	40	
Surrogate: Dibromofluoromethane	*0.0526*		*"*	*0.0500*		*105*	*70-130*			
Surrogate: 1,2-Dichloroethane-d4	*0.0524*		*"*	*0.0500*		*105*	*70-130*			
Surrogate: Toluene-d8	*0.0478*		*"*	*0.0500*		*95.5*	*70-130*			
Surrogate: 4-Bromofluorobenzene	*0.0505*		*"*	*0.0500*		*101*	*70-130*			

Laboratory Accreditations/Certifications

Code	Description	Number	Expires
C01	La Environmental Lab Accreditation Program	01960	06/30/2016
C02	National Environmental Lab Accreditation Program	TNI01397	06/30/2016
C03	Ms Dept of Health (Coliform)	MS00021	12/31/2015
C04	Ms Dept of Health (Drinking Water Certificate)	MS00021	12/31/2015
C05	Ms DEQ Lead Firm Certification	PBF-00000028	11/11/2016
C06	MsDEQ Asbestos Inspector : C.D. Bingham	ABI-00001348	03/13/2016
C07	MsDEQ Air Monitor : C.D. Bingham	AM-011572	03/12/2016
C08	MsDEQ Asbestos Inspector: C. W. Meins	ABI-00001821	10/08/2016
C09	MsDEQ Air Monitor : C.W. Meins	AM-011189	03/12/2016
C12	MsDEQ Asbestos Inspector : H.P. Howell	ABI-00001345	03/14/2016
C14	MsDEQ Lead Paint Inspector : C.D. Bingham	PBI-00003690	04/20/2016
C15	MsDEQ Lead Paint Inspector : C.W. Meins	PBI-00001740	04/20/2016

Report Definitions

TNC	Too Numerous To Count
DET	Analyte DETECTED
ND	Analyte NOT DETECTED at or above the minimum reporting limit
NR	Not Reported
RPD	Relative Percent Difference
ICV	Initial Calibration Verfiication
CCV	Continuing Calibration Verification Standard
SSV	Secondary Source Verfication Standard
LCS	Lab Control Spike - Lab matrix prepared with known concentration of analyte/s of interest analyzed by method.
MS	Matrix Spike - Sample prepared with known concentration of analyte/s of interest analyzed by method.
MSD	Matrix Spike Duplicate - Duplicate sample prepared with known concentration of anlayte/s of interest analyzed by method.
MRL	Minimum Reporting Limit
%REC	Percentage Recovery of known concentration added to matrix
Batch	Group of samples prepared for analysis not to exceed 20 samples.
Matrix	Material containing analyte/s of interest
Surrogate	Analyte added to sample to determine extraction efficiency of method.

Analyst Initials Key

FullName	Initials
Barbara K. McMillan	BKM
Brett S Fore	BSF
Sarah E. Tomek	SET
Tina Tomek	TPT

MICRO-METHODS LABORATORY, INC.
6500 Sunplex Drive, Ocean Springs, MS 39564
(228) 875-6420 FAX (228) 875-6423
www.micromethodslab.com

Chain of Custody Record

M-M Lab WO # 1601155

Company Name: Chemours
Address: 7685 Kiln Delisle Rd.
City: Pass Christian State: MS Zip: 39571
Phone: 228-255-2406
Fax:

Project Manager:
Purchase Order #:
Email Address :
Sampler Name Printed: Perry Schmidt
Sampler Name Signed: Perry Schmidt

Turn Around Time & Reporting
Our normal turn around time is 7-10 working days

__Normal
__Next Day*
__2nd Day*
__Other*______

*All rush order requests must be prior approved.

__Phone
__Mail
__Fax
__Email

List Analysis Requested

Project Name: Deepwell TOV
Project #:

Sample Identification	Sampling Date/Time	# of Containers	Sample Code	TOV
Deepwell TOV	01/10/16 1930	2		X

Note Special Instructions/Comments

Field pH _____ Collect Time______ ReadTime ______
Field D.O. _____Collect Time_______ Read Time ______
Field Temp._____Collect Time______ Read Time ______
QC Level: Level 1 ☐ Level 2 ☐ Level 3 ☐

Matrix Code: W= Water, S= Soil, O= Oil, L= Liquid, SL= Sludge
Sample Code: G= Grab C= Composite

Lab Use Only
Notes

	Signature	Printed Name	Company	Date	Time
Relinquished by	Allison Farve	ALLISON FARVE	CHEMOURS	1-16-16	1006
Received by		TDUPREE	MM	1-11-16	1006
Relinquished by		TDUPREE	MM	1-11-16	1557
Received by		Sarah Tomek	MM	1/11/16	1557
Relinquished by					
Received by					

Sample Rcvd. on Ice Yes ☐ No ☐
Thermometer # Cooler #
Receipt Temp (°C)______Sample ☐ Blank ☐
By: ____________________
Date & Time ______________

	Issue Date: 7/18/11	**Micro-Methods Laboratory Log-In Checklist**	
	Implementation Date: 7/18/11		DCN: F207
			Date Revised: 7-18-11
			Revision: 4

Client Chemours **WO** 1601155 **Shipped By** TD
Date/Time Received 1/11/16@ 1557 **Unpacked/Checked By** TD/ST

Cooler ID	Ice Present Yes/No	Temperature	Thermometer ID	Custody Sealed Yes/No	Custody Seal Intact Yes/No
#422	yes	3.5°c	T#3	no	n/a

If not iced, were samples received within one hour of collection? Yes ___ No___ N/A _X_
Temperature Blank Used Yes _____No _X_ If not, temperature taken from cooler ____or bottle _X_
Multi Cooler shipment: ID of samples in coolers that exceed 6°C___________________________

Custody Seals on Bottles Present Yes ___ No _X_
Containers Intact Yes _X_ No___
Proper Containers for Requested Analysis Yes _X_ No___

Correct Preservation Used for All Samples Yes _X_ No___
Adequate Sample for Analysis Requested Yes _X_ No___

Volatile Vials Headspace Greater than 6mm in Diameter Yes ___ No _X_ N/A ___

Chain of Custody Form Included Yes _X_ No___
Chain of Custody Form Complete Yes _X_ No___
Chain of Custody Form Properly Relinquished Yes _X_ No___
Field Sheets/Special Instructions Included Yes ___No___ N/A _X_
Samples Missing on COC or From Cooler Yes ___No _X_
Sample Container Labels Match COC Yes _X_ No___

Samples Received Within Holding Time Yes _X_ No___
Dept. Manager Notified of Rush/Short Holding Times Yes ___No___N/A _X_

Does work order meet Micro Methods sample acceptance criteria Yes _X_ No ___
Note: Samples that do not meet acceptance criteria must be documented in the Sample Rejection Log.

Client Contacted ______________**Contacted By** _________**Date/Time**__________
Client Instructions: Cancel Work Order _____
Proceed with Work Order ______**(Data will be qualified)**
Comments: ____

APPENDIX 6-3
ANALYTICAL REPORT FOR IRON CHLORIDE GRAB SAMPLE USED TO DEVELOP WASTE CHARACTERIZATION GIVEN IN SECTION 6.1.1

Mailing Address:
PO Box 1410
Ocean Springs, MS
39566-1410

6500 Sunplex Drive
Ocean Springs, MS 39564
228.875.6420 Phone
228.875.6423 Fax

June 21, 2016

Ed Ramos

Work Order # : 1605392

The Chemours Company FC LLC
974 Centre Rd.
Wilmington, DE 19805

Purchase Order #: 9900007395

RE: Special Iron Chloride Grab

Enclosed are Micro-Methods Laboratory, Inc. results of analyses performed on samples received 05/18/16 16:20. If you have any questions concerning this report, please feel free to contact the office.

Sincerely,

Harry P. Howell

Harry P. Howell

President
Micro-Methods Laboratory, Inc.

The Chemours Company FC LLC 974 Centre Rd. Wilmington DE, 19805	Project: Special Iron Chloride Grab Project Number: [none] Project Manager: Ed Ramos	**Reported:** 06/21/16 13:26

ANALYTICAL REPORT FOR SAMPLES

Sample ID	Laboratory ID	Matrix	Date/Time Sampled	Sampled by	Date/Time Received
Iron Chloride to Deepwell	1605392-01	Liquid	05/17/16 14:30	*Jeff Ulrich*	05/18/16 16:20

Sample Receipt Conditions

Date/Time Received:	5/18/2016 4:20:00PM	Shipped by:	Client Delivery
Received by:	Michelle M Gallegos	Submitted by:	Paul Reeder
Date/Time Logged:	5/19/2016 9:43:00AM	Logged by:	Michelle M Gallegos
Cooler ID:	**535**	**Receipt Temperature:**	5.0 °C

Custody Seals	*No*	*Received on Ice*	*No*
Containers Intact	*Yes*	*No Ice, Short Trip*	*No*
COC/Labels Agree	*Yes*	*Obvious Contamination*	*No*
Labels Complete	*No*	*Rush to meet HT*	*No*
COC Complete	*Yes*		

The Chemours Company FC LLC 974 Centre Rd. Wilmington DE, 19805	Project: Project Number: Project Manager:	Special Iron Chloride Grab [none] Ed Ramos	**Reported:** 06/21/16 13:26

CASE NARRATIVE SUMMARY

All reported results are within Micro-Methods Laboratory, Inc.defined laboratory quality control objectives unless detailed in narrative summary or identified as qualifications. NOTE: All results listed on this report are calculated on a wet weight basis (as received by the laboratory) unless otherwise noted in the analysis qualification sections.

Summary Comments:

pH tested at -0.37 - GMS 5/19/16

Inorganic Analysis Notes-BKM
Percent Sulfur analysis cancelled. Laboratory was unable to perform analysis.

See attached radiological results from Sub-Contract Laboratory

Sulfite, Titrimetric SM 4500 SO3 B-SM 4500-S03 2-B 2000

Qualifiers:

HT-02 At the time of receipt, this sample had already exceeded the recommended holding time.

Sulfite

1605392-01[Iron Chloride to Deepwell]

Total Metals-SW 6010B

Qualifiers:

CC-01 CCV above acceptance limits. Results reported from this calibration were below the reporting limits.

Antimony, Beryllium, Cadmium

1605392-01[Iron Chloride to Deepwell], 1605392-01RE1[Iron Chloride to Deepwell]

CC-03 CCV above acceptance limits. QC Results reported from this calibration within acceptance limits.

Antimony, Beryllium, Cadmium

6E23012-BLK1, 6E23012-BS1, 6E23012-BSD1, 6E23012-DUP1, 6E23012-DUP2

IC Results corrected for Interelement interference.

Boron, Cadmium, Selenium, Silver, Thallium

1605392-01[Iron Chloride to Deepwell], 6E23012-DUP1, 1605392-01RE1[Iron Chloride to Deepwell], 6E23012-DUP2

The Chemours Company FC LLC 974 Centre Rd. Wilmington DE, 19805	Project: Special Iron Chloride Grab Project Number: [none] Project Manager: Ed Ramos	**Reported:** 06/21/16 13:26

Iron Chloride to Deepwell

1605392-01 (Liquid)

Analyte	Result	MRL	Units	Dil	Batch	Analyst	Date Time Prepared	Date Time Analyzed	Method	Qualifiers
Classical Chemistry Parameters										
Cyanide (total)	ND	0.039	mg/kg	1	6E20039	DLW	05/20/16 08:40	05/22/16 08:40	SM 4500-CN E 1999	
Chloride	**146000**	23600	"	50000	6E20003	DLW	05/19/16 08:55	05/19/16 17:20	EPA 300.0	
Viscosity @70°C	**0.97**		centistokes	1	6E24030	GMS	05/20/16 12:15	05/20/16 13:00	Viscosity @70°C	
Fluoride	ND	0.150	mg/kg	"	6F03031	HAD	06/03/16 13:50	06/03/16 13:55	SM 4500-F D 1997	
Total Dissolved Solids	**158300**	1	"	"	6E23005	DLW	05/19/16 13:00	05/19/16 13:00	SM 2540 C 1997	
Sulfite	**15.0**	3.28	"	"	6E20017	GMS	05/20/16 09:30	05/20/16 10:00	SM 4500-S03 2-B 2000	HT-02
Phosphorus-Total	**47.2**	5.64	"	40	6E25006	HAD	05/24/16 09:00	05/25/16 11:07	SM 4500 P B5; SM 4500-P E	
Bromide	ND	159	"	200	6E20003	DLW	05/19/16 08:55	05/23/16 21:45	EPA 300.0	
Nitrate as N	ND	34.5	"	50	"	DLW	"	05/24/16 10:41	"	
Sulfate as SO4	ND	73.0	"	"	"	DLW	"	"	"	
Acidity	**197000**	1	"	1	6E19023	GMS	05/19/16 15:15	05/19/16 15:30	SM 2310B 1997	
pH	See case nar.		pH Units	"	6E19026	GMS	05/19/16 15:30	05/19/16 15:35	SW 846 9040	
Specific Gravity	**1.213**		g/mL	"	6E19024	GMS	05/19/16 14:30	05/19/16 14:40	SM 2710 F.	
Total Organic Carbon	ND	7.44	mg/kg	10	6F03030	DLW	06/03/16 08:00	06/03/16 14:09	SM 5310C 2000	
Total Suspended Solids	**3.5**	1.0	"	1	6E20028	DLW	05/20/16 09:45	05/20/16 16:30	SM 2540 D 1997	
Metals by EPA 6000 Series Methods ICP-AES										

The Chemours Company FC LLC
974 Centre Rd.
Wilmington DE, 19805

Project: Special Iron Chloride Grab
Project Number: [none]
Project Manager: Ed Ramos

Reported:
06/21/16 13:26

Iron Chloride to Deepwell

1605392-01 (Liquid)

Metals by EPA 6000 Series Methods ICP-AES

Analyte	Result	MRL	Units	Dil	Batch	Analyst	Date Time Prepared	Date Time Analyzed	Method	Qualifiers
Silicon	**33.4**	2.49	mg/kg	1	6E23012	SCH	05/23/16 10:00	06/02/16 15:47	EPA 6010B	
Aluminum	**1520**	2.49	"	"	"	SCH	"	06/02/16 14:55	SW 6010B	
Antimony	ND	2.49	"	"	"	SCH	"	"	"	CC-01
Arsenic	ND	2.49	"	"	"	SCH	"	"	"	
Barium	**31.5**	0.498	"	"	"	SCH	"	"	"	
Beryllium	ND	0.199	"	"	"	SCH	"	"	"	CC-01
Boron	**5.97**	2.49	"	"	"	SCH	"	"	"	IC
Calcium	**74.8**	2.49	"	"	"	SCH	"	"	"	
Chromium	**896**	0.498	"	"	"	SCH	"	"	"	
Cobalt	**16.7**	2.49	"	"	"	SCH	"	"	"	
Copper	**3.77**	0.498	"	"	"	SCH	"	"	"	
Lead	**69.8**	2.49	"	"	"	SCH	"	"	"	
Magnesium	**727**	2.49	"	"	"	SCH	"	"	"	
Potassium	**33.6**	14.9	"	"	"	SCH	"	"	"	
Nickel	**25.7**	1.99	"	"	"	SCH	"	"	"	
Selenium	**3.33**	2.49	"	"	"	SCH	"	"	"	IC
Silver	**2.44**	0.249	"	"	"	SCH	"	"	"	IC
Sodium	**3500**	4.98	"	"	"	SCH	"	"	"	
Strontium	**6.45**	2.49	"	"	"	SCH	"	"	"	
Thallium	ND	2.49	"	"	"	SCH	"	"	"	IC
Titanium	**1330**	2.49	"	"	"	SCH	"	"	"	
Vanadium	**378**	2.49	"	"	"	SCH	"	"	"	
Zinc	**83.7**	0.995	"	"	"	SCH	"	"	"	

Mercury by EPA 7000 Series Methods CVAAS

Analyte	Result	MRL	Units	Dil	Batch	Analyst	Date Time Prepared	Date Time Analyzed	Method	Qualifiers
Mercury	ND	0.025	mg/kg	1	6E20011	SCH	05/20/16 09:00	05/20/16 15:35	SW 7470A	

Metals Ferrous/Ferric Iron

Analyte	Result	MRL	Units	Dil	Batch	Analyst	Date Time Prepared	Date Time Analyzed	Method	Qualifiers
Ferric Iron	ND	1170	mg/kg	1	6E23013	SCH	05/23/16 10:00	06/02/16 14:18	EPA 6010B	
Ferrous Iron	**74000**	1170	"	"	"	SCH	"	"	"	

Iron Chloride to Deepwell

1605392-01RE1 (Liquid)

Analyte	Result	MRL	Units	Dil	Batch	Analyst	Date Time Prepared	Date Time Analyzed	Method	Qualifiers
Metals by EPA 6000 Series Methods ICP-AES										
Cadmium	ND	4.74	mg/kg	1	6E23012	SCH	05/23/16 10:00	06/02/16 14:05	SW 6010B	CC-01, IC
Iron	**74000**	23.7	"	"	"	SCH	"	"	"	
Manganese	**3550**	23.7	"	"	"	SCH	"	"	"	

Classical Chemistry Parameters - Quality Control

Batch 6E19023 - Default Prep GenChem

Duplicate (6E19023-DUP1) **Source: 1605392-01** ***Prepared & Analyzed: 05/19/16***

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Acidity	199000	1	mg/kg		197000			0.995	35	

Batch 6E19024 - Default Prep GenChem

Duplicate (6E19024-DUP1) **Source: 1605392-01** ***Prepared & Analyzed: 05/19/16***

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Specific Gravity	1.215		g/mL		1.213			0.165	200	

Batch 6E19026 - Default Prep GenChem

Duplicate (6E19026-DUP1) **Source: 1605392-01** ***Prepared & Analyzed: 05/19/16***

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
pH	See case nar.		pH Units		ee case na				10	

Batch 6E20003 - Default Prep GenChem

Blank (6E20003-BLK1) ***Prepared & Analyzed: 05/19/16***

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Chloride	ND	0.471	mg/kg							
Nitrate as N	ND	0.690	"							
Sulfate as SO4	ND	1.46	"							

Blank (6E20003-BLK2) ***Prepared: 05/19/16 Analyzed: 05/23/16***

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Bromide	ND	0.795	mg/kg							

LCS (6E20003-BS1) ***Prepared & Analyzed: 05/19/16***

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Chloride	4.02	0.471	mg/kg	4.00		101	90-110			
Nitrate as N	0.887	0.690	"	0.904		98.1	90-110			
Sulfate as SO4	4.11	1.46	"	4.00		103	88-117			

Classical Chemistry Parameters - Quality Control

Batch 6E20003 - Default Prep GenChem

LCS (6E20003-BS2) — *Prepared: 05/19/16 Analyzed: 05/23/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Bromide	10.4	0.795	mg/kg	10.0		104	90-110			

LCS Dup (6E20003-BSD1) — *Prepared & Analyzed: 05/19/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Chloride	3.99	0.471	mg/kg	4.00		99.8	90-110	0.774	20	
Nitrate as N	0.869	0.690	"	0.904		96.1	90-110	2.05	20	
Sulfate as SO4	4.19	1.46	"	4.00		105	88-117	1.97	20	

LCS Dup (6E20003-BSD2) — *Prepared: 05/19/16 Analyzed: 05/23/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Bromide	10.3	0.795	mg/kg	10.0		103	90-110	0.985	20	

Duplicate (6E20003-DUP1) — **Source: 1605392-01** — *Prepared & Analyzed: 05/19/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Chloride	150000	23600	mg/kg		146000			2.73	20	
Bromide	ND	159	"		ND				20	
Nitrate as N	ND	34.5	"		ND				20	
Sulfate as SO4	ND	73.0	"		ND				20	

Batch 6E20017 - Default Prep GenChem

Blank (6E20017-BLK1) — *Prepared & Analyzed: 05/20/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Sulfite	ND	3.28	mg/kg							

LCS (6E20017-BS1) — *Prepared & Analyzed: 05/20/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Sulfite	4.75	3.28	mg/kg	5.00		95.0	75-125			

LCS Dup (6E20017-BSD1) — *Prepared & Analyzed: 05/20/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Sulfite	4.75	3.28	mg/kg	5.00		95.0	75-125	0.00	30	

Classical Chemistry Parameters - Quality Control

Batch 6E20017 - Default Prep GenChem

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Duplicate (6E20017-DUP1)	**Source: 1605392-01**					***Prepared & Analyzed: 05/20/16***				
Sulfite	18.0	3.28	mg/kg		15.0			18.2	30	

Batch 6E20028 - Default Prep GenChem

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Blank (6E20028-BLK1)						***Prepared & Analyzed: 05/20/16***				
Total Suspended Solids	ND	1.0	mg/kg							
LCS (6E20028-BS1)						***Prepared & Analyzed: 05/20/16***				
Total Suspended Solids	83.0	1.0	mg/kg	100		83.0	75-125			
LCS Dup (6E20028-BSD1)						***Prepared & Analyzed: 05/20/16***				
Total Suspended Solids	85.0	1.0	mg/kg	100		85.0	75-125	2.38	25	
Duplicate (6E20028-DUP1)	**Source: 1605392-01**					***Prepared & Analyzed: 05/20/16***				
Total Suspended Solids	3.5	1.0	mg/kg		3.5			0.00	5	

Batch 6E20039 - Default Prep GenChem

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Blank (6E20039-BLK1)					***Prepared: 05/20/16 Analyzed: 05/22/16***					
Cyanide (total)	ND	0.039	mg/kg							
LCS (6E20039-BS1)					***Prepared: 05/20/16 Analyzed: 05/22/16***					
Cyanide (total)	0.421		mg/kg	0.400		105	83-110			
LCS Dup (6E20039-BSD1)					***Prepared: 05/20/16 Analyzed: 05/22/16***					
Cyanide (total)	0.392		mg/kg	0.400		98.0	83-110	7.13	15	

Classical Chemistry Parameters - Quality Control

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Batch 6E20039 - Default Prep GenChem										
Duplicate (6E20039-DUP1)	**Source: 1605392-01**				***Prepared: 05/20/16 Analyzed: 05/22/16***					
Cyanide (total)	ND	0.039	mg/kg		ND				20	
Batch 6E23005 - Default Prep GenChem										
Blank (6E23005-BLK1)					***Prepared & Analyzed: 05/19/16***					
Total Dissolved Solids	ND	1	mg/kg							
LCS (6E23005-BS1)					***Prepared & Analyzed: 05/19/16***					
Total Dissolved Solids	94		mg/kg	104		90.4	79.6-105			
LCS Dup (6E23005-BSD1)					***Prepared & Analyzed: 05/19/16***					
Total Dissolved Solids	98		mg/kg	104		94.2	79.6-105	4.17	15	
Duplicate (6E23005-DUP1)	**Source: 1605392-01**				***Prepared & Analyzed: 05/19/16***					
Total Dissolved Solids	159000	1	mg/kg		158300			0.441	5	
Batch 6E24030 - Default Prep GenChem										
Duplicate (6E24030-DUP1)	**Source: 1605392-01**				***Prepared & Analyzed: 05/20/16***					
Viscosity @70°C	0.972		centistokes		0.973			0.103	30	
Batch 6E25006 - Default Prep GenChem										
Blank (6E25006-BLK1)					***Prepared: 05/24/16 Analyzed: 05/25/16***					
Phosphorus-Total	ND	0.141	mg/kg							

Classical Chemistry Parameters - Quality Control

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Batch 6E25006 - Default Prep GenChem										
LCS (6E25006-BS1)						***Prepared: 05/24/16 Analyzed: 05/25/16***				
Phosphorus-Total	2.08		mg/kg	2.00		104	85-110			
LCS Dup (6E25006-BSD1)						***Prepared: 05/24/16 Analyzed: 05/25/16***				
Phosphorus-Total	2.08		mg/kg	2.00		104	85-110	0.00	20	
Duplicate (6E25006-DUP1)	**Source: 1605392-01**					***Prepared: 05/24/16 Analyzed: 05/25/16***				
Phosphorus-Total	46.4	5.64	mg/kg		47.2			1.71	15	
Batch 6F03030 - Default Prep GenChem										
Blank (6F03030-BLK1)						***Prepared & Analyzed: 06/03/16***				
Total Organic Carbon	ND	0.74	mg/kg							
LCS (6F03030-BS1)						***Prepared & Analyzed: 06/03/16***				
Total Organic Carbon	5.44	0.74	mg/kg	5.00		109	75-125			
LCS Dup (6F03030-BSD1)						***Prepared & Analyzed: 06/03/16***				
Total Organic Carbon	5.40	0.74	mg/kg	5.00		108	75-125	0.716	35	
Duplicate (6F03030-DUP1)	**Source: 1605392-01**					***Prepared & Analyzed: 06/03/16***				
Total Organic Carbon	ND	7.44	mg/kg		ND				30	
Batch 6F03031 - Default Prep GenChem										
Blank (6F03031-BLK1)						***Prepared & Analyzed: 06/03/16***				
Fluoride	ND	0.150	mg/kg							

Classical Chemistry Parameters - Quality Control

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Batch 6F03031 - Default Prep GenChem										
LCS (6F03031-BS1)						*Prepared & Analyzed: 06/03/16*				
Fluoride	0.160		mg/kg	0.200		80.0	75-125			
LCS Dup (6F03031-BSD1)						*Prepared & Analyzed: 06/03/16*				
Fluoride	0.150		mg/kg	0.200		75.0	75-125	6.45	30	
Duplicate (6F03031-DUP1)	**Source: 1605392-01**					*Prepared & Analyzed: 06/03/16*				
Fluoride	ND	0.150	mg/kg		ND				35	

Metals by EPA 6000 Series Methods ICP-AES - Quality Control

Batch 6E23012 - EPA 3010A

Blank (6E23012-BLK1) *Prepared: 05/23/16 Analyzed: 06/02/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Silicon	0.995	2.50	mg/kg							
Aluminum	ND	2.50	"							
Antimony	ND	2.50	"							CC-03
Arsenic	ND	2.50	"							
Barium	ND	0.500	"							
Beryllium	ND	0.200	"							CC-03
Boron	ND	2.50	"							
Cadmium	ND	0.500	"							CC-03
Calcium	ND	2.50	"							
Chromium	ND	0.500	"							
Cobalt	ND	2.50	"							
Copper	ND	0.500	"							
Iron	ND	2.50	"							
Lead	ND	2.50	"							
Magnesium	ND	2.50	"							
Manganese	ND	2.50	"							
Potassium	ND	15.0	"							
Nickel	ND	2.00	"							
Selenium	ND	2.50	"							
Silver	ND	0.250	"							
Sodium	ND	5.00	"							
Strontium	ND	2.50	"							
Thallium	ND	2.50	"							
Titanium	ND	2.50	"							
Vanadium	ND	2.50	"							
Zinc	ND	1.00	"							

LCS (6E23012-BS1) *Prepared: 05/23/16 Analyzed: 06/02/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Aluminum	9.67	2.50	mg/kg	10.0		96.7	85-115			
Antimony	10.4	2.50	"	10.0		104	85-115			CC-03
Arsenic	9.62	2.50	"	10.0		96.2	85-115			
Barium	10.1	0.500	"	10.0		101	85-115			
Beryllium	11.4	0.200	"	10.0		114	85-115			CC-03
Boron	9.83	2.50	"	10.0		98.3	85-115			
Cadmium	10.5	0.500	"	10.0		105	85-115			CC-03
Calcium	10.9	2.50	"	10.0		109	85-115			
Chromium	10.0	0.500	"	10.0		100	85-115			
Cobalt	10.4	2.50	"	10.0		104	85-115			
Copper	9.79	0.500	"	10.0		97.9	85-115			
Iron	10.1	2.50	"	10.0		101	85-115			
Lead	10.4	2.50	"	10.0		104	85-115			
Magnesium	9.44	2.50	"	10.0		94.4	85-115			
Manganese	10.6	2.50	"	10.0		106	85-115			
Potassium	19.6	15.0	"	20.0		98.0	85-115			
Nickel	9.93	2.00	"	10.0		99.3	85-115			

Metals by EPA 6000 Series Methods ICP-AES - Quality Control

Batch 6E23012 - EPA 3010A

LCS (6E23012-BS1) *Prepared: 05/23/16 Analyzed: 06/02/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Selenium	9.40	2.50	mg/kg	10.0		94.0	85-115			
Silver	5.00	0.250	"	5.00		100	85-115			
Sodium	19.8	5.00	"	20.0		99.0	85-115			
Strontium	10.1	2.50	"	10.0		101	85-115			
Thallium	8.85	2.50	"	10.0		88.5	85-115			
Titanium	10.3	2.50	"	10.0		103	85-115			
Vanadium	10.6	2.50	"	10.0		106	85-115			
Zinc	9.03	1.00	"	10.0		90.3	85-115			

LCS (6E23012-BS2) *Prepared: 05/23/16 Analyzed: 06/02/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Silicon	26.9	2.50	mg/kg	25.0		107	85-115			

LCS Dup (6E23012-BSD1) *Prepared: 05/23/16 Analyzed: 06/02/16*

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Aluminum	9.87	2.50	mg/kg	10.0		98.7	85-115	2.02	20	
Antimony	10.4	2.50	"	10.0		104	85-115	0.112	20	CC-03
Arsenic	9.62	2.50	"	10.0		96.2	85-115	0.0596	20	
Barium	10.2	0.500	"	10.0		102	85-115	1.07	20	
Beryllium	11.3	0.200	"	10.0		113	85-115	1.09	20	CC-03
Boron	9.65	2.50	"	10.0		96.5	85-115	1.89	20	
Cadmium	10.6	0.500	"	10.0		106	85-115	0.854	20	CC-03
Calcium	10.7	2.50	"	10.0		107	85-115	2.00	20	
Chromium	9.98	0.500	"	10.0		99.8	85-115	0.572	20	
Cobalt	10.5	2.50	"	10.0		105	85-115	1.32	20	
Copper	9.82	0.500	"	10.0		98.2	85-115	0.346	20	
Iron	10.1	2.50	"	10.0		101	85-115	0.693	20	
Lead	9.97	2.50	"	10.0		99.7	85-115	3.86	20	
Magnesium	9.77	2.50	"	10.0		97.7	85-115	3.47	20	
Manganese	10.7	2.50	"	10.0		107	85-115	0.691	20	
Nickel	9.96	2.00	"	10.0		99.6	85-115	0.297	20	
Selenium	9.80	2.50	"	10.0		98.0	85-115	4.26	20	
Silver	4.98	0.250	"	5.00		99.7	85-115	0.330	20	
Strontium	10.3	2.50	"	10.0		103	85-115	1.83	20	
Thallium	9.35	2.50	"	10.0		93.5	85-115	5.47	20	
Titanium	10.1	2.50	"	10.0		101	85-115	1.45	20	
Vanadium	10.5	2.50	"	10.0		105	85-115	0.159	20	
Zinc	8.88	1.00	"	10.0		88.8	85-115	1.72	20	

The Chemours Company FC LLC 974 Centre Rd. Wilmington DE, 19805	Project: Special Iron Chloride Grab Project Number: [none] Project Manager: Ed Ramos	**Reported:** 06/21/16 13:26

Metals by EPA 6000 Series Methods ICP-AES - Quality Control

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Batch 6E23012 - EPA 3010A										
LCS Dup (6E23012-BSD2)					*Prepared: 05/23/16*	*Analyzed: 06/02/16*				
Silicon	27.0	2.50	mg/kg	25.0		108	85-115	0.484	20	
Duplicate (6E23012-DUP1)	**Source: 1605392-01**				*Prepared: 05/23/16*	*Analyzed: 06/02/16*				
Silicon	33.1	2.48	mg/kg		33.4			1.03	200	
Aluminum	1530	2.48	"		1520			0.578	20	
Antimony	ND	2.48	"		ND				20	CC-03
Arsenic	ND	2.48	"		ND				20	
Barium	31.9	0.496	"		31.5			1.12	20	
Beryllium	ND	0.199	"		ND				20	CC-03
Boron	5.66	2.48	"		5.97			5.40	20	IC
Cadmium	ND	0.496	"		ND				20	CC-03
Calcium	75.3	2.48	"		74.8			0.667	20	
Chromium	905	0.496	"		896			0.951	20	
Cobalt	16.8	2.48	"		16.7			0.460	20	
Copper	3.77	0.496	"		3.77			0.0710	20	
Lead	70.0	2.48	"		69.8			0.267	20	
Magnesium	719	2.48	"		727			1.15	20	
Potassium	34.1	14.9	"		33.6			1.52	20	
Nickel	26.0	1.99	"		25.7			1.14	20	
Selenium	3.13	2.48	"		3.33			6.42	20	IC
Silver	2.43	0.248	"		2.44			0.268	20	IC
Sodium	3460	4.96	"		3500			1.26	20	
Strontium	6.46	2.48	"		6.45			0.0584	20	
Thallium	ND	2.48	"		ND				20	IC
Titanium	1310	2.48	"		1330			1.41	20	
Vanadium	374	2.48	"		378			1.19	20	
Zinc	84.1	0.993	"		83.7			0.513	20	

Metals by EPA 6000 Series Methods ICP-AES - Quality Control

Batch 6E23012 - EPA 3010A

Duplicate (6E23012-DUP2) **Source: 1605392-01RE** ***Prepared: 05/23/16 Analyzed: 06/02/16***

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Cadmium	4.10	4.55	mg/kg		3.79			7.78	20	CC-03, IC
Iron	73700	22.8	"		74000			0.330	20	
Manganese	3510	22.8	"		3550			1.34	20	

Mercury by EPA 7000 Series Methods CVAAS - Quality Control

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Batch 6E20011 - SW 7470A										
Blank (6E20011-BLK1)						***Prepared & Analyzed: 05/20/16***				
Mercury	ND	0.015	mg/kg							
LCS (6E20011-BS1)						***Prepared & Analyzed: 05/20/16***				
Mercury	0.101	0.015	mg/kg	0.100		101	85-115			
LCS Dup (6E20011-BSD1)						***Prepared & Analyzed: 05/20/16***				
Mercury	0.101	0.015	mg/kg	0.100		101	85-115	0.00	25	
Duplicate (6E20011-DUP1)	**Source: 1605392-01**					***Prepared & Analyzed: 05/20/16***				
Mercury	ND	0.025	mg/kg		ND				20	
Matrix Spike (6E20011-MS1)	**Source: 1605392-01**					***Prepared & Analyzed: 05/20/16***				
Mercury	0.167	0.025	mg/kg	0.166	ND	100	75-125			

The Chemours Company FC LLC
974 Centre Rd.
Wilmington DE, 19805

Project: Special Iron Chloride Grab
Project Number: [none]
Project Manager: Ed Ramos

Reported:
06/21/16 13:26

Metals Ferrous/Ferric Iron - Quality Control

Analyte	Result	MRL	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Qualifiers
Batch 6E23013 - EPA 3010A										
Blank (6E23013-BLK1)					*Prepared: 05/23/16*		*Analyzed: 06/02/16*			
Ferrous Iron	ND	2.50	mg/kg							
LCS (6E23013-BS1)					*Prepared: 05/23/16*		*Analyzed: 06/02/16*			
Ferrous Iron	0.201	2.50	mg/kg	0.200		101	85-115			
LCS Dup (6E23013-BSD1)					*Prepared: 05/23/16*		*Analyzed: 06/02/16*			
Ferrous Iron	0.203	2.50	mg/kg	0.200		101	85-115	0.693	20	
Duplicate (6E23013-DUP1)	**Source: 1605392-01**				*Prepared: 05/23/16*		*Analyzed: 06/02/16*			
Ferrous Iron	73900	1210	mg/kg		74000			0.151	20	

Certified Analyses Included in this Report

Analyte	Certification Code
SM 5310C 2000 in Liquid	
Total Organic Carbon	C01,C02

Laboratory Accreditations/Certifications

Code	Description	Number	Expires
C01	*La Environmental Lab Accreditation Program*	*01960*	*06/30/2016*
C02	*National Environmental Lab Accreditation Program*	*TNI01397*	*06/30/2016*
C03	*Ms Dept of Health (Coliform)*	*MS00021*	*12/31/2016*
C04	*Ms Dept of Health (Drinking Water Certificate)*	*MS00021*	*12/31/2016*
C05	*Ms DEQ Lead Firm Certification*	*PBF-00000028*	*11/11/2016*
C06	*MsDEQ Asbestos Inspector : C.D. Bingham*	*ABI-00001348*	*03/10/2017*
C07	*MsDEQ Air Monitor : C.D. Bingham*	*AM-011572*	*04/22/2017*
C08	*MsDEQ Asbestos Inspector: C. W. Meins*	*ABI-00001821*	*10/08/2016*
C09	*MsDEQ Air Monitor : C.W. Meins*	*AM-011189*	*04/22/2017*
C12	*MsDEQ Asbestos Inspector : H.P. Howell*	*ABI-00001345*	*03/10/2017*
C14	*MsDEQ Lead Paint Inspector : C.D. Bingham*	*PBI-00003690*	*03/18/2017*
C15	*MsDEQ Lead Paint Inspector : C.W. Meins*	*PBI-00001740*	*03/18/2017*

Report Definitions

TNC	Too Numerous To Count
DET	Analyte DETECTED
ND	Analyte NOT DETECTED at or above the minimum reporting limit
NR	Not Reported
RPD	Relative Percent Difference
ICV	Initial Calibration Verfiication
CCV	Continuing Calibration Verification Standard
SSV	Secondary Source Verfication Standard
LCS	Lab Control Spike - Lab matrix prepared with known concentration of analyte/s of interest analyzed by method.
MS	Matrix Spike - Sample prepared with known concentration of analyte/s of interest analyzed by method.
MSD	Matrix Spike Duplicate - Duplicate sample prepared with known concentration of anlayte/s of interest analyzed by method.
MRL	Minimum Reporting Limit
%REC	Percentage Recovery of known concentration added to matrix
Batch	Group of samples prepared for analysis not to exceed 20 samples.
Matrix	Material containing analyte/s of interest
Surrogate	Analyte added to sample to determine extraction efficiency of method.

Analyst Initials Key

FullName	Initials
Barbara K. McMillan	BKM
Dortha L. Wells	DLW
Gayle M. Sparling	GMS
Heather A Denham	HAD
Michelle M Gallegos	MMG
Samantha C. Hall	SCH
Tina Tomek	TPT

MICRO-METHODS
LABORATORY, INC.

6500 Sunplex Drive, Ocean Springs, MS 39564
39564 (228) 875-6420 FAX (228) 875-6423
www.micromethodslab.com

Chain of Custody Record

EPA Lab ID# MS00021
LELAP ID # 01960
TNI ID # TNI01397

M-M Lab WO # 1605392

Company Name: THE CHEMOURS Company FC
Address: 7685 Kiln DeLisle Road
City: Pass Christian State: MS Zip: 39571
Phone: 228 255 4931
Fax: 228 255 2153

Project Manager: ED RAMOS
Purchase Order #: 9900007395
Email Address : Ed.g.Ramos@chemours.com
Sampler Name Printed: Jeff Ulrich
Sampler Name Signed: Jeff Ulrich

Turn Around Time & Reporting

Our normal turn around time is 10 working days

X Normal
__Next Day*
__2nd Day*
__Other*______

*All rush order requests must be prior approved.

__Phone
__Mail
__Fax
__Email

Lab Analysis Requested

Project Name: Special Iron Chloride Gen
Project #: /

Sample Identification	Sampling Date/Time	Matrix Code	# of Containers	Grab (G) or Composite (C)	Preservative:
IRON Chloride TO DEEPWell	5/17/16 1430	W	3	G	SEE ATTACHED

Field Testing / QC Reporting

Field pH _____ Collect Time______ ReadTime ______
Field D.O. _____Collect Time_______ Read Time ______
Field Temp_____Collect Time_______ Read Time______
QC Level: Level 1 ☐ Level 2 ☐ Level 3 ☐

Matrix Codes:

W = Water
DW = Drinking Water
S = Solid
SO = Soil
SE = Sediment
L = Liquid
A = Air
O = Oil
SL = Sludge

Preservation Codes:

1= Sulfuric Acid
2= Phosphoric Acid
3=Sodium Hydroxide
4=Zinc Acetate
5=Zinc Acetate & Sodium Hydroxide
6=Nitric Acid
7=Sodium Thiosulfate
8=Hydrochloric Acid
9=Sodium Bisulfate

Special Instructions / Comments

	Print Name	Signature	Company	Date	Time
Relinquished by	PAUL REEDER	Paul Reeder	CHEMOURS	5-18-16	14:15
Received by	T DUPREE		MM	5-18-16	14:15
Relinquished by	T DUPREE		MM	5-18-16	1620
Received by	Michelle Gallegos	Michelle M Gallegos	MM	5/18/16	1620
Relinquished by					
Received by					

Received on Ice? Yes_____ No____
Receipt Temp (°C)_____Sample_____Blank_____
Cooler #_______ Thermometer #___________
Date & Time _______________
By: ___________________________

DCN# F316 Rev.#2

1405342

RAMOS, EDUARDO G

From:	RAMOS, EDUARDO G
Sent:	Friday, April 22, 2016 12:01 PM
To:	Tina Tomek <ttomek@micromethodslab.com> (ttomek@micromethodslab.com)
Cc:	FINKES, TAMMY M; DOUTY, DANIEL TELFORD
Subject:	Need special analyses on grab sample of iron chloride (same as monthly composite except it's a grab sample)

Tina,

THE ANALYTICAL REPORT will tell what you could DO, AND COULDN'T DO.

I will call you to discuss these analytes for a sample of iron chloride (same as the monthly deepwell composite, except that this is a grab sample) that I would like to send you. The list of analytes is extensive because I need a fairly comprehensive characterization of the material for a permit application. As you know, the sample is very corrosive, and thus you may not be able to run a given test without damaging your equipment.

Some analytes are "gotta have" and some are not, and I will do the "wanna haves" depending on price. Feel free to rearrange the list to properly group the analytes that can be measured by the same lab test. I don't know how to do that.

Please call me.

Ed Ramos
(228) 255-4931

Cell (228) 323-0765

Parameter	Measuring Conditions	Possible Range of Values	Units	Wanna or Gotta To be filled out on the phone
Specific Gravity	70 F	1.05 – 1.35	g/ml or g/cc	
pH		minus 2 to 1	s. u.	
Weight % HCl		1 to 6	Weigh %	
Viscosity at	70 C		cP	
Viscosity at	100 C		cP	
Viscosity at	130 C		cP	
Resistivity			ohm-cm	
Total Dissolved Solids		175,000 – 325,000	mg/l	
Total Organic Carbon		Less than 7.44	mg/kg	
Total Suspended Solids		1 to 10	mg/kg	
Acidity		150,000 to 250,000	mg/kg	
~~Hardness~~	NOT NEEDED			
~~Carbonate~~	NOT NEEDED			
Chloride		150,000 to 250,000	mg/kg	
Bromide				
Fluoride				
Cyanide		0 to 1		
Total Sulfur				
Sulfate				
Sulfite				

COPY

1405342

Phosphate or Phosphorus		50 to 150		
Nitrate				
Mercury		0 to 0.01	mg/kg	
Fe+3		2 to 4 wt.% FeCl3	Weight %	
Fe+2		10 to 25 wt.% FeCl2	Weight %	
Total Metals				
Chromium		700 to 1,200	mg/kg	
Iron		40,000 to 100,000		
Lead		1 to 300		
Vanadium		100 to 400		
Antimony		0 to 3		
Arsenic		0 to 2		
Barium		0 to 40		
Beryllium		0 to 10		
Cadmium		0 to 2		
Cobalt		0 to 40		
Copper		0 to 20		
Manganese		1500 to 5000		
Nickel		0 to 60		
Selenium		0 to 20		
Silver		0 to 10		
Thallium		0 to 5		
Zinc		50 to 200		
Calcium		10 to 100		
Magnesium		1,000 to 2,000		
Sodium		1,000 to 2,000		
Potassium				
Aluminum		1,000 to 2,000		
Boron				
Titanium		1,000 to 3,000		
Strontium		1,000 to 2,000		
~~Cesium~~		10 to 100		
~~Lanthanum~~		0 to 30		
~~Neodymium~~		0 to 30		
~~Niobium~~		100 to 500		
Silicon		0 to 30		
~~Zirconium~~		100 to 500		
Radium 226		1 to 2 pCi/g		
Radium 228		5 to 10 pCi/g		
Thorium 232		10 to 100 mg/l		
Uranium 238		1 to 10 mg/l		

	Issue Date: 7/18/11	**Micro-Methods Laboratory Log-In Checklist**	
	Implementation Date: 7/18/11		DCN: F207
			Date Revised: 7-18-11
			Revision: 4

Client Chemours **WO** 1605392 **Shipped By** TD
Date/Time Received 5/18/16 @ 1620 **Unpacked/Checked By** TD / BT

Cooler ID	Ice Present Yes/No	Temperature	Thermometer ID	Custody Sealed Yes/No	Custody Seal Intact Yes/No
#535	yes	5.0°c	T#3	no	n/a

If not iced, were samples received within one hour of collection? Yes ___ No ___ [✓ N/A]
Temperature Blank Used Yes ___ [✓ No] If not, temperature taken from cooler ___ or [✓ bottle]
Multi Cooler shipment: ID of samples in coolers that exceed 6°C ___

Custody Seals on Bottles Present Yes ___ [✓ No]
Containers Intact [✓ Yes] No ___
Proper Containers for Requested Analysis [✓ Yes] No ___

Correct Preservation Used for All Samples [✓ Yes] No ___
Adequate Sample for Analysis Requested [✓ Yes] No ___

Volatile Vials Headspace Greater than 6mm in Diameter Yes ___ No ___ [✓ N/A]

Chain of Custody Form Included [✓ Yes] No ___
Chain of Custody Form Complete [✓ Yes] No ___
Chain of Custody Form Properly Relinquished [✓ Yes] No ___
Field Sheets/Special Instructions Included Yes ___ No ___ [✓ N/A]
Samples Missing on COC or From Cooler Yes ___ [✓ No]
Sample Container Labels Match COC [✓ Yes] No ___

Samples Received Within Holding Time [✓ Yes] No ___
Dept. Manager Notified of Rush/Short Holding Times Yes ___ No ___ [✓ N/A]

Does work order meet Micro Methods sample acceptance criteria [✓ Yes] No ___
Note: Samples that do not meet acceptance criteria must be documented in the Sample Rejection Log.

Client Contacted ___ **Contacted By** ___ **Date/Time** ___
Client Instructions: Cancel Work Order ___
Proceed with Work Order ___ **(Data will be qualified)**
Comments: ___

2609 North River Road, Port Allen, Louisiana 70767
(800) 401-4277 -- FAX (225) 381-2996

ARS International, LLC

Laboratory Analysis Report

ARS1-16-01238

Prepared for:

Micro-Methods Lab, Inc.

Tina Tomek
6500 Sunplex Dr
Ocean Springs, MS 39564

ttomek@micromethodslab.com

Phone: 228.875.6420
Fax: 228.875.6423

Project Manager Review

Management Review

Contact Person: Questions regarding this analytical report should be addressed to:

Project Manager
ProjectManagers@amrad.com

Phone: 225.381.2991
Fax: 225.381.2996

LELAP Cert# 01949

ARS
INTERNATIONAL

2609 North River Road, Port Allen, Louisiana 70767
1 (800) 401-4277 FAX (225) 381-2996

ARS Sample Delivery Group: ARS1-16-01238
Client Sample ID: 1605392-01
Sample Collection Date: 05/17/16
Sample Matrix: Aqueous
Percent Solids: N/A

Request or PO Number: N/A
ARS Sample ID: ARS1-16-01238-001
Date Received: 05/23/16
Report Date: 06/20/16

Radiochemistry

Analysis Description	Analysis Results	CSU +/- 2 s	MDC	DLC	CRDL	Qual	Analysis Units	Method	Analysis Date/Time	Analysis Technician	Tracer/Chem Recovery
Th-232	5607.955	884.299	100.517	30.049	NP		pCi/L	ARS-031/Eichrom ACW-10	06/16/16 13:33	BSCHREITER	4%
U-238	1386.717	179.698	16.414	7.156	NP		pCi/L	ARS-026/Eichrom ACW-03	06/16/16 13:33	BSCHREITER	73%
Be-7	53.849	53.848	88.500	44.250	NP	U	pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
Bi-212	3898.600	269.490	82.300	41.150	NP		pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
Bi-214	747.540	51.056	22.700	11.350	NP		pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
Pa-234	169.920	22.412	29.900	14.950	NP		pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
Pb-210	1443.800	229.500	195.000	97.500	NP		pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
Pb-214	840.990	72.909	24.900	12.450	NP		pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
Ra-226	2715.600	274.060	246.000	123.000	NP		pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
Ra-228	5388.400	335.160	29.500	14.750	NP		pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
Sc-46	-5.017	3.754	6.100	3.050	NP	U	pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
Th-228	6062.700	393.710	26.000	13.000	NP		pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
Tl-208	1969.100	125.410	11.900	5.950	NP		pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
U-235	27.972	50.668	83.500	41.750	NP	U	pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
Total NORM Gamma	31146.621	N/A	N/A	N/A	NP		pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A
Total NORM Activity	53534.089	N/A	N/A	N/A	NP		pCi/L	ARS-006/EPA 901.1	06/03/16 15:19	BSCHREITER	N/A

Project Manager Review

LELAP Certificate# 01949

INTERNATIONAL

QC Results per Analytical Batch

Analytical Batch	**ARS1-B16-00920**
SDG	**ARS1-16-01238**
Analysis	**Thorium in Water**
Analysis Test Method	**ARS-031/Eichrom ACW-10**
Analysis Code	**ASP-A-008**
Report Units	**pCi/L**

Acceptable QC Performance Ranges

QC Sample Type	Performance Items and Ranges		
Laboratory Control Sample	**Recovery (%):**	**> 75**	**< 125**
Matrix Spike	**Recovery (%):**	**> 60**	**< 140**
Duplicate	**Replicate Error Ratio (RER):**		**< 1**
	Duplicate Error Ratio (DER):		**< 3**
	Relative Percent Difference (RPD %):		**≤ 25**

Laboratory Control Sample

Analysis Date 06/16/16 13:33 **Analysis Technician** ANABATILAN

Analysis Batch Sample ID	QC Type	Analyte	Results	CSU (2s)	Expected Value	LCS Rec (%)	MDC
ARS1-B16-00920-01	**LCS**	TH-230	4.691	0.916	5.856	80.1	0.441

Duplicate RER/DER/RPD

Analysis Date 06/16/16 13:33 **Analysis Technician** ANABATILAN

Analyte	Result LCS	CSU LCS (2s)	Results LCSD	CSU LCSD (2s)	RER	DER	RPD
TH-230	4.691	0.916	5.055	0.658	0.232	0.633	7.5

Method Blank

Analysis Date 06/16/16 13:33 **Analysis Technician** ANABATILAN

Analysis Batch Sample ID	QC Type	Analyte	Results	CSU (2s)	MDC	Qual
ARS1-B16-00920-03	**MBL**	TH-228	0.007	0.012	0.023	U
ARS1-B16-00920-03	**MBL**	TH-230	0.005	0.019	0.038	U
ARS1-B16-00920-03	**MBL**	TH-232	0.003	0.010	0.023	U

Project Manager Review

LELAP Certificate# 01949

ARS INTERNATIONAL

QC Results per Analytical Batch

Analytical Batch	**ARS1-B16-00922**
SDG	**ARS1-16-01238**
Analysis	**Uranium in Water**
Analysis Test Method	**ARS-026/Eichrom ACW-03-15**
Analysis Code	**ASP-A-024**
Report Units	**pCi/L**

Acceptable QC Performance Ranges

QC Sample Type	Performance Items and Ranges		
Laboratory Control Sample	**Recovery (%):**	**> 75**	**< 125**
Matrix Spike	**Recovery (%):**	**> 60**	**< 140**
Duplicate	**Replicate Error Ratio (RER):**		**< 1**
	Duplicate Error Ratio (DER):		**< 3**
	Relative Percent Difference (RPD %):		**≤ 25**

Laboratory Control Sample

Analysis Date 06/16/16 13:32 **Analysis Technician** ANABATILAN

Analysis Batch Sample ID	QC Type	Analyte	Results	CSU (2s)	Expected Value	LCS Rec (%)	MDC
ARS1-B16-00922-01	**LCS**	U-238	12.736	1.599	13.117	97.1	0.039

Duplicate RER/DER/RPD

Analysis Date 06/16/16 13:32 **Analysis Technician** ANABATILAN

Analyte	Result LCS	CSU LCS (2s)	Results LCSD	CSU LCSD (2s)	RER	DER	RPD
U-238	12.736	1.599	12.355	1.554	0.121	0.335	3.0

Method Blank

Analysis Date 06/16/16 13:33 **Analysis Technician** ANABATILAN

Analysis Batch Sample ID	QC Type	Analyte	Results	CSU (2s)	MDC	Qual
ARS1-B16-00922-03	**MBL**	U-234	-0.024	0.030	0.081	U
ARS1-B16-00922-03	**MBL**	U-235	-0.007	0.010	0.047	U
ARS1-B16-00922-03	**MBL**	U-238	-0.018	0.025	0.071	U

Project Manager Review

LELAP Certificate# 01949

INTERNATIONAL

QC Results per Analytical Batch

Analytical Batch	**ARS1-B16-00902**
SDG	**ARS1-16-01238**
Analysis	**Gamma Spec (Aqueous)**
Analysis Test Method	**ARS-006/EPA 901.1**
Analysis Code	**GAM-A-015**
Report Units	**pCi/L**

Acceptable QC Performance Ranges

QC Sample Type	Performance Items and Ranges		
Laboratory Control Sample	**Recovery (%):**	**> 75**	**< 125**
Matrix Spike	**Recovery (%):**	**> 60**	**< 140**
Duplicate	**Replicate Error Ratio (RER):**		**< 1**
	Duplicate Error Ratio (DER):		**< 3**
	Relative Percent Difference (RPD %):		**≤ 25**

Laboratory Control Sample

Analysis Date 06/03/16 12:55 **Analysis Technician** WJS

Analysis Batch Sample ID	QC Type	Analyte	Results	CSU (2s)	Expected Value	LCS Rec (%)	MDC
ARS1-B16-00902-01	**LCS**	AM-241	42656.000	3068.300	43729.730	97.5	582.300
ARS1-B16-00902-01	**LCS**	CO-60	66284.000	2731.300	68162.162	97.2	833.900
ARS1-B16-00902-01	**LCS**	CS-137	51750.000	2475.300	51810.811	99.9	380.500

Duplicate RER/DER/RPD

Analysis Date 06/03/16 13:08 **Analysis Technician** WJS

Analyte	Result LCS	CSU LCS (2s)	Results LCSD	CSU LCSD (2s)	RER	DER	RPD
AM-241	42656.000	3068.300	44537.000	3355.300	0.293	0.811	4.3
CO-60	66284.000	2731.300	67558.000	2772.900	0.231	0.642	1.9
CS-137	51750.000	2475.300	53237.000	2298.200	0.312	0.863	2.8

Method Blank

Analysis Date 06/03/16 15:19 **Analysis Technician** WJS

Analysis Batch Sample ID	QC Type	Analyte	Results	CSU (2s)	MDC	Qual
ARS1-B16-00902-03	**MBL**	AM-241	-6.196	1480.100	3.950	U
ARS1-B16-00902-03	**MBL**	CO-60	-0.783	1.883	2.280	U
ARS1-B16-00902-03	**MBL**	CS-137	0.127	1.106	1.880	U

Project Manager Review

LELAP Certificate# 01949

Notes (Case Narrative):

Comments:

1.0) All MDA/MDC values are calculated on a sample specific basis.
2.0) Soil and Sludge analysis are reported on a wet basis or an as received basis unless otherwise indicated.
3.0) Data in this report are within the limits of uncertainty specified in the reference method unless otherwise specified.
4.0) Modified analysis procedures are procedures that are modified to meet the certain specifications. An example may be the use of a water method to analyze a solid matrix due to the lack of an officially recognized procedure for the analysis of the solid matrix. Modified analyses are indicated by the subsequent addition of "m" to the procedure number (i.e. 900.0M).
5.0) Total activity is actually total gamma activity and is determined utilizing the prominent gamma emitters from the naturally occurring radioactive decay chains and other prominent radioactive nuclides. Total activity may be lower than the actual total activity due to the extent of secular equilibrium achieved in the various decay chains at the time of analysis. The total activity is not representative of nuclides that emit solely alpha or beta particles.
6.0) Ra-228 is determined via secular equilibrium with its daughter, Actinium 228 (Gamma Spectroscopy only).
7.0) U-238 is determined via secular equilibrium with its daughter, Thorium 234 (Gamma Spectroscopy only).
8.0) All gamma spectroscopy was performed utilizing high purity germanium detectors (**HPGe**).
9.0) ARS makes every attempt to match sample density to calibrated density; however, in some cases, it is not practical or possible to do so and data results may be affected (Gamma Spectroscopy only).
10.0) Gamma spectroscopy results are calculated values based on the **ORTEC**® GammaVision ENV32 Analysis Engine.
11.0) ACLASS DOD and ISO 17025 certification applies only to the following analytes and methods: Gross Alpha and Gross Beta (EPA 900, SM7110B&C, SW846 9310); Radium 226 (EPA 903, EPA 903.1, SM 7500 Ra-B, SW846 9315); Radium 228 (EPA 904, SM 7500 Ra-B SW846 9320); Iodine-131(EPA 901.1); Uranium by ICPMS (EPA 200.8); Strontium 89/90 (EPA 905, Eichrom SRW01, HASL 300 Sr-03-RC); Tritium (EPA 906, EPA 906M); Gamma Emitters (EPA 901.1, SM7120B, HASL 300 Ga-01-R); Americium-241, Curium 242/244, Plutonium 239/240 and 241, Thorium 228/230/232, Uranium 234/233 and 238 (Eichrom ACW03 VBS); Lead 210 (HASL 300 Pb-01-RC, Eichrom OTW01); Polonium 210 (HASL 300 Po-01-RC, HASL 300 Po-02-RC); Technetium-99 (Eichrom TCW02, Eichrom TCS01M).

Method References:

1.0) **EPA 600/4-80-032**; Prescribed Procedures for the Measurements of Radioactivity in Drinking Water, August 1980.
2.0) **Standard Methods for the Examination of Water and Wastewater** (On-Line Edition)
3.0) **EPA SW-846**; Test Methods for Evaluating Solid Waste, (On-Line edition)
4.0) **EPA 600/4/79-020**; Methods for Chemical Analysis of Water and Waste, March 1983.
5.0) **HASL 300;** The Procedures Manual of the Environmental Measurements Laboratory, Volume I, 28th Edition February, 1997.

Definitions:

CRDL	Contract Required Detection Limit
CSU	Combined Standard Uncertainty
DLC	Decision Level Concentration (ANSI N42.23) or critical level
DO	Duplicate Original
DUP	Method Duplicate
LCS/LCSD	Laboratory Control Sample/Laboratory Control Sample Duplicate
MDA	Minimum Detectable Activity
MDC	(Minimum Detectable Concentration) minimum concentration of the analyte that ARS can detect utilizing the specific analysis
MBL	Method Blank
MS/MSD	Matrix Spike/Matrix Spike Duplicate
N/A	Not Applicable
NP	Not Provided
NR	Not Referenced

Data Qualifiers:

B	The analyte is found in both the associated method blank and the sample. This flag indicates probable blank contamination.
D	Sample analysis accomplished through dilution.
J	The reported result is an estimated value (e.g., matrix interference was observed or the analyte was detected at a concentration outside the quantitation range).
Q	One or more quality control criteria failed (e.g., LCS recovery, surrogate spike recovery, or CCV recovery).
S	Spike
***SC**	Subcontracted out to another qualified laboratory
U	Activity is below the MDC or MDL

Technical Note Report

ABatch **ARS1-B16-00920**
Analysis Code **ASP-A-008**
Procedure No **ARS-031**
Matrix **AQ**

#	Date	Dept	Technical Note	User ID
1	06/17/2016 7:28 AM	COUNTROOM	B16-00920-01 and -04 gave low tracer recoveries. B16-00920-04 shows unidentified peaks at higher energy than the ROI for Th-228. WJS 6-17-16	BSCHREITER
2	06/20/2016 2:11 PM	REPORTING	Very strong suspicions that the low tracer recoveries are due to the high concentrations of salt(s) in the sample.	RVARNELL

ARS International
Baton Rouge Laboratory

Technical Note Report

ABatch	**ARS1-B16-00922**
Analysis Code	**ASP-A-024**
Procedure No	**ARS-026**
Matrix	**AQ**

#	Date	Dept	Technical Note	User ID
1	06/17/2016 7:23 AM	COUNTROOM	B16-00922-04 gave FWHMs greater than 100 keV. WJS 6-17-16	BSCHREITER

SUBCONTRACT ORDER

Micro-Methods Laboratory, Inc.

1605392

SENDING LABORATORY:	**RECEIVING LABORATORY:**
Micro-Methods Laboratory, Inc.	American Radiation Services
6500 Sunplex Drive	2609 North River Road
Ocean Springs, MS 39564	Port Allen, LA 70767
Phone: 228.875.6420	Phone :(800) 401-4277
Fax: 228.875.6423	Fax: -
Project Manager: Barbara K. McMillan	

Analysis	**Due**	**Expires**	**Laboratory ID**	**Comments**
Sample ID: 1605392-01	**Liquid**	**Sampled:05/17/16 14:30**	[redacted]	
Radium,Total 226 & 228 by 90	05/26/16 23:59	06/14/16 14:30		
Containers Supplied: 1000mL Plastic (C)				

* also, please analyze for Thorium 232 &
Uranium 238.

Thanks

Sarah Jomek	5/19/16 @ 1630	UPS	5/19/16 @ 1630
Released By	Date	Received By	Date
UPS	5/20/16 @		5-25-16 1831
Released By	Date	Received By	Date

APPENDIX 6-4

RESPONSES TO EPA REGION 4 QUESTIONS ON 2012 APPLICATION TO MODIFY MAY 5, 2000 HWDIR EXEMPTION – OCTOBER 31, 2013

BCC:

Paper Copies
File EC12-G2K
E. Ramos

PDF Copies via e-mail
Alice L. Andrepont
Guy V. Johnson
William C. Collins
Nicole T. Newell
Russell T. Farquhar
Daniel T. Douty
Lisa M. Wisniewski
Tim J. Becnel

DUPONT®

October 21, 2013

DuPont Titanium Technologies
P O Box 430
7685 Kiln DeLisle Road
Pass Christian, MS 39571

Certified Mail No. 7010 1870 0002 6358 1173
Receipt Return Requested

Fred McManus, Chief
Ground Water and UIC Section
USEPA Region 4
Atlanta Federal Center
61 Forsyth Street, SW
Atlanta, Georgia 30303-8960

RE: Questions regarding DuPont DeLisle's request to modify Land Ban Exemption Petition

Dear Mr. McManus:

Thanks for your review of our request to modify the existing Land Ban Exemption for our facility. This letter contains the responses to the questions in your letter of September 26, 2013.

Question #1

Explain how the proposed fiberglass reinforced expansion joints and epoxy cement to be used in the injection well will be as protective as a traditional (i.e., typical cement) injection well system.

Response to Question #1

In June, 2012, DuPont asked Halliburton to conduct tests to demonstrate the compatibility of WellLock™ and Epseal® epoxy cements with the injectate from the DeLisle facility. The results are shown in Enclosure #1 consisting of Halliburton's March 5, 2013 report entitled "Chemical Stability of WellLock™ resin to $FeCl_3$/HCl waste fluid." Halliburton concludes that both the WellLock™ epoxy cement proposed for use in Well No. 6 and Epseal® epoxy cement (used in Wells Nos. 2, 3, 4 and 5) are compatible with DeLisle's injectate, but that "WellLock™ has superior mechanical properties and is able to tolerate higher compressive strain." This report supports the statements made regarding WellLock™ resin on pages 6-8 and 6-9 of the August, 2012 submission.

However, there will not be a fiberglass reinforced expansion joint in the protective casing of the proposed Well No. 6. This well will not have the fiberglass transition joint that is used in Wells Nos. 2, 3, 4 and 5. Enclosure #2 is an update to Figure 5-17 (Injection Well No. 6 Well Schematic) showing that the transition joint in Well No. 6 will be made from Hastelloy C-276 rather than FRP Blue Box 2500. The carbon steel casing will screw into a Hastelloy C-276 joint which then screws into the Titanium Grade 7 lower portion of the protective casing.

Question #2
Submit the Material Safety Data Sheets (MSDS) for the epoxy cement.

Response to Question #2

The MSDS for WellLock™ R1 resin is Enclosure #3. The use of this resin requires WellLock™ H1 hardener, and WellLock™ Microsand. The MSDS for H1 and Microsand are also provided.

Question #3
Submit the results of compatibility testing of the fiberglass reinforced expansion joints and epoxy cement with the injectate from this facility.

Response to Question #3

Enclosure #1 cited above provides the result of compatibility testing for the WellLock R1 epoxy-resin cement with the injectate for the DeLisle facility.

Well No. 6 will not have the fiberglass transition joint that is used in Wells Nos. 2, 3, 4 and 5.

Question #4
One of the products from this facility, titanium dioxide, has been classified as possibly carcinogenic to humans (Group 2B) by the International Agency for Research on Cancer. What information does DuPont have regarding the health effects of titanium oxide?

Answer to Question #4

Enclosure #4 is a document providing DuPont's position on the IARC classification. DuPont's position is further supported in the statement from the Titanium Dioxide Manufacturers Association (TDMA) that is part of this enclosure. The TDMA is a global association of titanium dioxide manufacturers in which DuPont is a member.

The DuPont position document also contains a link to IARC's Monograph 93; the titanium dioxide section of the monograph is provided as Enclosure #5. Section 6.1 "Cancer in humans" (page 275 of the monograph) contains this statement: **"There is *inadequate evidence* in humans for the carcinogenicity of titanium dioxide."**

Enclosure #6 contains MSDS documents for two DuPont titanium dioxide (Ti-Pure®) products. The first is the MSDS for Paint Coatings product grades; the DeLisle facility manufactures grades R-706, R-900, and R-902+. The second MSDS is for Plastics product grades; the DeLisle facility manufactures grades R-101, R-104, R-105 and R-350. Section 11 of each MSDS (page 6) discusses the IARC classification.

DuPont places paramount importance on the health and safety of its employees, its contractors, and the community at large. DuPont strongly believes that it is prudent to take all possible precautions against potential workplace exposures. Therefore, DuPont supports the continuous improvement of procedures and processes to minimize any potential exposure.

There is no titanium dioxide present in the injectate of the DeLisle facility.

Thanks in advance for your consideration of this response. If you need additional information, please call me on (228) 255-4931.

Very truly yours,

Eduardo Ramos

Eduardo Ramos
Sr. Consultant, Environmental
DuPont DeLisle Plant

Enclosures

Enclosure #1
Halliburton Report March 5, 2013 "Chemical Stability of WellLock™ resin to $FeCl_3$/HCl waste fluid"

Enclosure #2
Update to Figure 5-17 – Injection Well No. 6 Well Schematic

Enclosure #3
MSDS for Halliburton WellLock™ R1 resin, H1 hardener, and Microsand

Enclosure #4
DuPont position on IARC classification of titanium dioxide

Enclosure #5
Titanium Dioxide section of "IARC Monograph on the Evaluation of Carcinogenic Risk in Humans: Carbon Black, Titanium Dioxide and Talc." World Health Organization. Volume 93; pages 193-276. January, 2011.

Enclosure #6
DuPont MSDS for titanium dioxide (Ti-Pure®) Paint Coatings grades and Plastics grades

cc: James O. Sparks, Manager
Underground Injection Control
MDEQ OPC ECED
P. O. Box 2261
Jackson, MS 39225

Enclosure #1

Halliburton Report March 5, 2013
“Chemical Stability of WellLock™ Resin to $FeCl_3$/HCl Waste Fluid”

HALLIBURTON

NORTH BELT TECHNOLOGY CENTER – HOUSTON, TX

CEMENTING APPLIED SCIENCES AND PROCESSES

PROJECT REPORT

TO: Robert Darbe
Cementing Applied Sciences and Processes - Manager

DATE: March 5, 2013

PROJECT NUMBER: HTZP1001091
WellLock 2012

TITLE: Chemical stability of WellLock™ resin to $FeCl_3$/HCl waste fluid.

PREPARED BY: Greg Hundt

PURPOSE

This purpose of this investigation is to determine the suitability of WellLock™ resin as the primary isolation barrier in chemical disposal wells for a $FeCl_3$ in hydrochloric acid ($FeCl_3$/HCl) waste stream, provided by DuPont, in comparison to previous resin systems (EPSEAL®).

CONCLUSION

Chemical immersion and mechanical property testing indicates WellLock™ resin is suitable for use as a primary isolation barrier in the disposal of $FeCl_3$/HCl waste stream provided. Both resin systems retained their strength and exhibited significant dimensional stability after immersion in the $FeCl_3$/HCl waste stream over a period 4 weeks. However, WellLock™ resin was shown to have superior mechanical properties and was able to tolerate much higher degrees of compressive strain in comparison to the EPSEAL® resin system evaluated.

PROCEDURES

The resin formulations are shown in Table 1. The components of the Epseal® resin formulations were mixed in the following order:

1. Epseal® RE
2. Plastic Fixer
3. SSA-1
4. LC Catalyst

Components of the WellLock™ formulations were mixed in the following order:

1. WellLock™ R-1 resin
2. WellLock™ H-1 Hardener
3. Microsand

Cylinders of each formulation were cured at 150°F for 48 hours in plastic molds. The cylinders were cut to a 2:1 aspect ratio. Nominal cylinder diameters and heights were 1.14 inches and 2.28 inches, respectively. The heights and diameters of each individual cylinder are listed in Table 4 and Table 5.

Table 1. Components of the resin formulations.

Formulation	Epseal®	WellLock™
Components	Epseal® RE Resin (457.7 g) Plastic Fixer (2.16 g) Epseal® LC Catalyst (10.2 g) SSA-1 (700 g)	WellLock™ R1 (400g) WellLock™ H1 (108g) Microsand (328 g)

Control samples of each formulation were kept at ambient temperature and pressure. Four samples of each resin formulation were submerged in the $FeCl_3/HCl$ solution and sealed in an Inconel autoclave at 150°F and 2000 psi. Samples were removed for testing every 7 days. The samples were washed with water, wiped clean, and allowed to air dry before testing. These samples were weighed, dimensions measured, and tested for compressive strength. Compressive strength testing was stopped at either resin failure or 40% compression relative to initial cylinder height, whichever came earlier. For tests in which the resin did not fail, the stress at 40% compression is reported. We do not report experimental variation as only one cylinder was tested for each individual data point.

RESULTS AND DISCUSSION

No visual changes occurred in the WellLock™ or Epseal® samples over 4 weeks (Figure 1 and Figure 2). Both WellLock™ and Epseal® formulations retained their compressive strength over the course of this experiment (Table 2), indicating a high degree of resistance to chemical attack by the $FeCl_3/HCl$ waste fluid provided.

Figure 1. Exposed (l) and control (r) sample of WellLock™ resin.

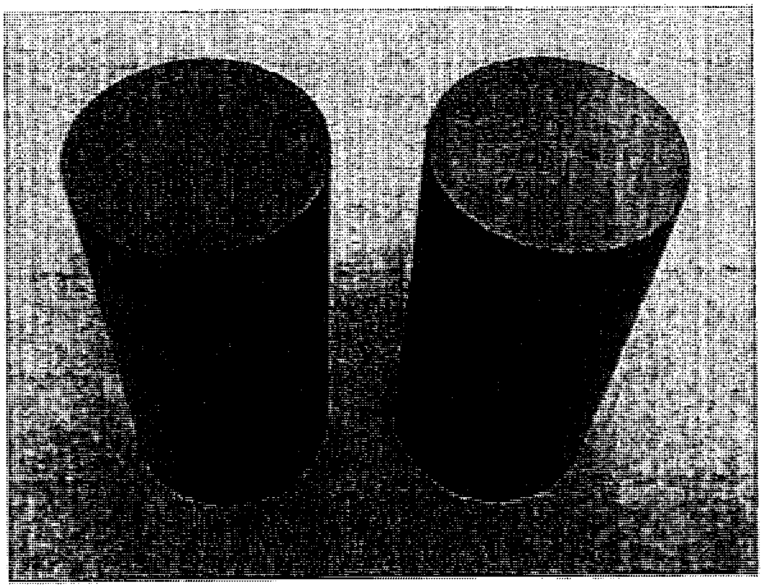


Figure 2. Exposed (l) and control (r) sample of Epseal® resin.

Table 2. Compressive strength (psi) of the resin formulations exposed to $FeCl_3$/HCl solutions over four weeks.

Time (weeks)	Property	Epseal®	WellLock™
0	Compressive Strength (psi)	13801	22228
	Deformation (%)	12.5	36
1	Compressive Strength (psi)	12275	25240
	Deformation (%)	11.7	40
2	Compressive Strength (psi)	11480	24017
	Deformation (%)	10.6	38
3	Compressive Strength (psi)	11088	21490
	Deformation (%)	11.5	30
4	Compressive Strength (psi)	11151	23662
	Deformation (%)	11.7	36

Table 3 shows the weight change of the resin formulations over four weeks, which is attributed to nominal water absorption. No significant change was observed in the diameter or height of the cylinders over the course of this test. Table 4 shows the cylinder heights, and Table 5 shows the cylinder diameters over the course of the test.

Table 3. Cylinder weights of the resin formulations over four weeks soaking in FeCl$_3$/HCl.

Composition	Initial (g)	1 Week (g)	2 Weeks (g)	3 Weeks (g)	4 Weeks (g)	Change (g)
Epseal®	65.35	65.56				0.21
Epseal®	66.29		66.58			0.29
Epseal®	65.64			65.99		0.35
Epseal®	64.82				65.18	0.36
WellLock™	58.46	58.63				0.17
WellLock™	56.35		56.57			0.26
WellLock™	57.44			57.72		0.32
WellLock™	57.37				57.7	0.37

Table 4. Cylinder heights of the resin formulations over four weeks soaking in FeCl$_3$/HCl.

Composition	Initial (in)	1 Week (in)	2 Weeks (in)	3 Weeks (in)	4 Weeks (in)	Change (in)
Epseal®	2.313	2.312				-0.001
Epseal®	2.346		2.350			0.004
Epseal®	2.317			2.345		0.028
Epseal®	2.297				2.299	0.002
WellLock™	2.320	2.368				0.048
WellLock™	2.279		2.285			0.006
WellLock™	2.315			2.341		0.026
WellLock™	2.321				2.325	0.004

Table 5. Cylinder diameters of the resin formulations over four weeks soaking in $FeCl_3$/HCl.

Composition	Initial (in)	1 Week (in)	2 Weeks (in)	3 Weeks (in)	4 Weeks (in)	Change (in)
Epseal®	1.141	1.140				-0.001
Epseal®	1.145		1.146			0.001
Epseal®	1.143			1.141		-0.002
Epseal®	1.143				1.136	-0.007
WellLock™	1.142	1.143				0.001
WellLock™	1.142		1.144			0.002
WellLock™	1.140			1.143		0.003
WellLock™	1.142				1.141	-0.001

Respectfully submitted,

By ____________
Greg Hundt
HALLIBURTON

cc: Paul Jones
Jeff Karcher
David Bolado
Brittney Guillory

Electronic Laboratory Notebook Reference

User ID	Experiment
H110865	WellLock-011

REPORT DATA FORM HEADER

PROJECT (NETWORK NUMBER):
HTZP1001091

AUTHOR:
Greg Hundt

TYPE*:
S

*Final – **F**
Supplement – **S**
Progress Report – **P**

VERSION NUMBER*:
1

DATE WRITTEN:
March 5, 2013

TITLE: **Chemical stability of WellLock™ resin to $FeCl_3$/HCl waste fluid.**

KEYWORDS:

WellLock	***Resin***	

ABSTRACT

This purpose of this investigation is to determine the suitability of WellLock™ resin as the primary isolation barrier in chemical disposal wells for a $FeCl_3$ in hydrochloric acid ($FeCl_3$/HCl) waste stream, provided by DuPont, in comparison to previous resin systems (EPSEAL®).

Chemical immersion and mechanical property testing indicates WellLock™ resin is suitable for use as a primary isolation barrier in the disposal of $FeCl_3$/HCl waste stream provided. Both resin systems retained their strength and exhibited significant dimensional stability after immersion in the $FeCl_3$/HCl waste stream over a period 4 weeks. However, WellLock™ resin was shown to have superior mechanical properties and was able to tolerate much higher degrees of compressive strain in comparison to the EPSEAL® resin system evaluated.

DATE APPROVED:

APPROVER SIGNATURE:

APPROVAL FOR EXTERNAL TO CASP GROUP (Yes/No)

Tech Service Reports Process:
Please send to Trissa Joseph for review and approval and then Trissa will send to Robert for 2nd Approval for release or upload to CWI/Matrix

<u>Quality Reports Process:</u>
Please send to Sam Lewis for review and approval and then Sam will send to Robert for 2nd Approval for release or upload to CWI/Matrix

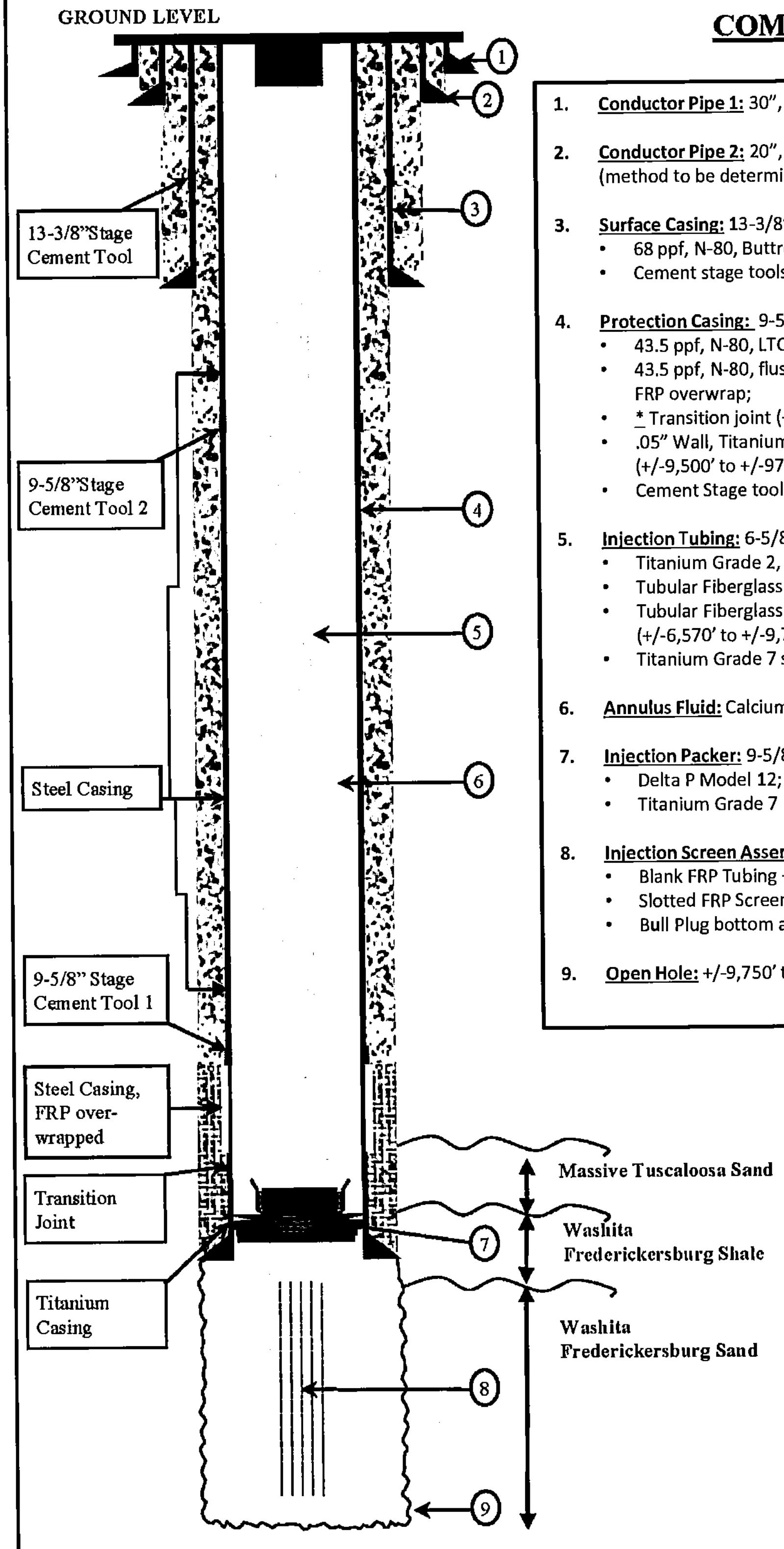
<u>Project Reports Process:</u>
Please send to your Team Lead for review and approval – if Project is above 100K and meets threshold may need to go to Legal for review and approval for release or upload to CWI/Matrix

Enclosure #2

Update to Figure 5-17 of the August, 2012 Request to Modify the Land Ban Exemption Petition for the DuPont DeLisle Facility Cited in Harrison County, Mississippi

E. I. Du Pont de Nemours & Co.

DeLisle Plant Well No. 6
Proposed Wellbore Schematic
(Washita Fredericksburg Completion)



COMPLETION DETAILS

All depths are approximate

1. **Conductor Pipe 1:** 30", Surface to +/125', driven to refusal
2. **Conductor Pipe 2:** 20", Surface to +/-500', set in drilled hole with cement (method to be determined)
3. **Surface Casing:** 13-3/8", Surface to +/-3,750', in 17-1/2" hole:
   - 68 ppf, N-80, Buttress thread connection
   - Cement stage tools +/-1,700'
4. **Protection Casing:** 9-5/8", Surface to +/-9,750', in 12-1/4" hole:
   - 43.5 ppf, N-80, LTC thread connection (0 to +/-8,670');
   - 43.5 ppf, N-80, flush, integral join connection (+/-8,760' to +/-9,470'),with FRP overwrap;
   - * Transition joint (+/-9,470' to +/-9,500') (see below);
   - .05" Wall, Titanium Gr7 (or Gr 16), lush integral join Connection (+/-9,500' to +/-9750');
   - Cement Stage tools at +/-4,000' and +/8,670'
5. **Injection Tubing:** 6-5/8", Surface to +/- 9,700'
   - Titanium Grade 2, 0.375" wall landing joint @ surface,
   - Tubular Fiberglass Blue Box-2500, non upset end (+/-10' to +/-6,570');
   - Tubular Fiberglass Blue Box-2500, internal upset end (+/-6,570' to +/-9,700';)
   - Titanium Grade 7 seal assembly @ +/-9,700'
6. **Annulus Fluid:** Calcium Chloride Brine at +/-10.6 ppg:
7. **Injection Packer:** 9-5/8" X 5-3/4", at +/- 9,700':
   - Delta P Model 12;
   - Titanium Grade 7
8. **Injection Screen Assembly:** 6-5/8", +/-9,700' to +/-10,200'
   - Blank FRP Tubing +/-9,700' to +/-9,760'
   - Slotted FRP Screen +/-9,760' to +/-10,200'
   - Bull Plug bottom at +/-10,200'
9. **Open Hole:** +/-9,750' to +/-10,200', Drilled 8-1/2"

Notes / Definitions:

* Transition Joint Material:
Hastelloy C276
- ppf - pound per foot
- LTC- long thread and collar
- FRP- fiberglass reinforced pipe

▨ - Low density cement
░ - Standard cement
▦ - Epoxy cement

Figure 5-17 Injection Well No. 6 Well Schematic

Sandia Technologies, LLC
6731 Theall Road Houston, TX 77066 USA
Tel: (832) 286-0471 Fax: (832) 286-0477

Drawn by: DES	Date: October 2013	*Drawing not to scale*

Enclosure #3

Material Safety Data Sheet for WellLock™ R1 Resin, WellLock™ H1 Hardener, and WellLock™ Microsand

HALLIBURTON

MATERIAL SAFETY DATA SHEET

Product Trade Name: **WellLock R1**

Revision Date: 30-Jan-2013

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product Trade Name:	WellLock R1
Synonyms:	None
Chemical Family:	Resin Blend
Application:	Resin

Manufacturer/Supplier

Halliburton Energy Services, Inc.
P.O. Box 1431
Duncan, Oklahoma 73536-0431
Emergency Telephone: (281) 575-5000

Prepared By

Chemical Compliance
Telephone: 1-580-251-4335
e-mail: fdunexchem@halliburton.com

2. COMPOSITION/INFORMATION ON INGREDIENTS

Substances	CAS Number	PERCENT	ACGIH TLV-TWA	OSHA PEL-TWA
Epoxy resin		60 - 100%	Not applicable	Not applicable
Butyl glycidyl ether	2426-08-6	10 - 30%	3 ppm	50 ppm

3. HAZARDS IDENTIFICATION

Hazard Overview

May cause eye, skin, and respiratory irritation. May be harmful if swallowed. May be absorbed through the skin. May cause allergic skin reaction. Combustible.

4. FIRST AID MEASURES

Inhalation

If inhaled, remove to fresh air. If not breathing give artificial respiration, preferably mouth-to-mouth. If breathing is difficult give oxygen. Get medical attention.

Skin

In case of contact, immediately flush skin with plenty of soap and water for at least 15 minutes. Get medical attention. Remove contaminated clothing and launder before reuse.

Eyes

In case of contact, or suspected contact, immediately flush eyes with plenty of water for at least 15 minutes and get medical attention immediately after flushing.

Ingestion

Do NOT induce vomiting. Give nothing by mouth. Obtain immediate medical attention.

Notes to Physician

Not Applicable

5. FIRE FIGHTING MEASURES

Flash Point/Range (F):	173
Flash Point/Range (C):	78
Flash Point Method:	PMCC
Autoignition Temperature (F):	Not Determined
Autoignition Temperature (C):	Not Determined
Flammability Limits in Air - Lower (%):	Not Determined
Flammability Limits in Air - Upper (%):	Not Determined

Fire Extinguishing Media	Water fog, carbon dioxide, foam, dry chemical. Do NOT spray pool fires directly with water. A solid stream of water directed into hot burning liquid can cause splattering.
Special Exposure Hazards	Use water spray to cool fire exposed surfaces. Closed containers may explode in fire. Decomposition in fire may produce toxic gases.
Special Protective Equipment for Fire-Fighters	Full protective clothing and approved self-contained breathing apparatus required for fire fighting personnel.
NFPA Ratings:	Health 3, Flammability 2, Reactivity 0
HMIS Ratings:	Health 3*, Flammability 2, Physical Hazard 0 , PPE: X

6. ACCIDENTAL RELEASE MEASURES

Personal Precautionary Measures	Use appropriate protective equipment.
Environmental Precautionary Measures	Prevent from entering sewers, waterways, or low areas.
Procedure for Cleaning / Absorption	Remove ignition sources and work with non-sparking tools. Contain spill with sand or other inert materials. Scoop up and remove. Isolate spill and stop leak where safe.

7. HANDLING AND STORAGE

Handling Precautions	Avoid contact with eyes, skin, or clothing. Avoid breathing vapors. Avoid breathing mist. Wash hands after use. Launder contaminated clothing before reuse. Ground and bond containers when transferring from one container to another.
Storage Information	Keep from heat, sparks, and open flames. Keep container closed when not in use. Store in a cool, dry location. Store in a well ventilated area. Product has a shelf life of 60 months.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering Controls	Use in a well ventilated area. Local exhaust ventilation should be used in areas without good cross ventilation.
Respiratory Protection	If engineering controls and work practices cannot keep exposure below occupational exposure limits or if exposure is unknown, wear a NIOSH certified, European Standard EN 149, or equivalent respirator when using this product. Selection of and instruction on using all personal protective equipment, including respirators, should be performed by an Industrial Hygienist or other qualified professional. Organic vapor respirator.
Hand Protection	Impervious rubber gloves.
Skin Protection	Rubber apron.

Eye Protection	Chemical goggles; also wear a face shield if splashing hazard exists.
Other Precautions	Eyewash fountains and safety showers must be easily accessible.

9. PHYSICAL AND CHEMICAL PROPERTIES

Physical State:	Liquid
Color:	Light yellow
Odor:	Characteristic
pH:	Not Determined
Specific Gravity @ 20 C (Water=1):	1.14
Density @ 20 C (lbs./gallon):	9.5
Bulk Density @ 20 C (lbs/ft3):	Not Determined
Boiling Point/Range (F):	Not Determined
Boiling Point/Range (C):	Not Determined
Freezing Point/Range (F):	Not Determined
Freezing Point/Range (C):	Not Determined
Vapor Pressure @ 20 C (mmHg):	Not Determined
Vapor Density (Air=1):	Not Determined
Percent Volatiles:	Not Determined
Evaporation Rate (Butyl Acetate=1):	Not Determined
Solubility in Water (g/100ml):	Insoluble
Solubility in Solvents (g/100ml):	Not Determined
VOCs (lbs./gallon):	Not Determined
Viscosity, Dynamic @ 20 C (centipoise):	Not Determined
Viscosity, Kinematic @ 20 C (centistokes):	Not Determined
Partition Coefficient/n-Octanol/Water:	Not Determined
Molecular Weight (g/mole):	Not Determined

10. STABILITY AND REACTIVITY

Stability Data:	Stable
Hazardous Polymerization:	Will Not Occur
Conditions to Avoid	Keep away from heat, sparks and flame.
Incompatibility (Materials to Avoid)	Strong acids. Strong alkalis.
Hazardous Decomposition Products	Aldehydes. Carbon monoxide and carbon dioxide.
Additional Guidelines	Not Applicable

11. TOXICOLOGICAL INFORMATION

Principle Route of Exposure	Eye or skin contact, inhalation.
Inhalation	May cause respiratory irritation. Excessive inhalation causes headache, dizziness, nausea and incoordination.
Skin Contact	May cause severe skin irritation. May cause an allergic skin reaction.
Eye Contact	May cause severe eye irritation.
Ingestion	May be harmful if swallowed.
Aggravated Medical Conditions	Skin disorders. Eye ailments.

Chronic Effects/Carcinogenicity	This product contains a suspected carcinogen.
Other Information	None known.

Toxicity Tests

Oral Toxicity:	Not determined
Dermal Toxicity:	Not determined
Inhalation Toxicity:	Not determined
Primary Irritation Effect:	Not determined
Carcinogenicity	Not determined
Genotoxicity:	Suspected of causing genetic defects
Reproductive / Developmental Toxicity:	Not determined

12. ECOLOGICAL INFORMATION

Mobility (Water/Soil/Air)	Not determined
Persistence/Degradability	Not determined
Bio-accumulation	Not determined

Ecotoxicological Information

Acute Fish Toxicity:	Not determined
Acute Crustaceans Toxicity:	Not determined
Acute Algae Toxicity:	Not determined
Chemical Fate Information	Not determined
Other Information	Not applicable

13. DISPOSAL CONSIDERATIONS

Disposal Method	Disposal should be made in accordance with federal, state, and local regulations.
Contaminated Packaging	Follow all applicable national or local regulations.

14. TRANSPORT INFORMATION

Land Transportation

DOT
Not restricted

DOT (Bulk)
UN1866, Resin Solution, Combustible Liquid, III
Classified in accordance with 49 CFR 172.101(d)(4)

Canadian TDG

Not restricted

ADR
Not restricted

Air Transportation

ICAO/IATA
Not restricted

Sea Transportation

IMDG
Not restricted

Other Transportation Information

Labels:	None

15. REGULATORY INFORMATION

US Regulations

US TSCA Inventory	All components listed on inventory or are exempt.
EPA SARA Title III Extremely Hazardous Substances	Not applicable
EPA SARA (311,312) Hazard Class	Acute Health Hazard
EPA SARA (313) Chemicals	This product does not contain a toxic chemical for routine annual "Toxic Chemical Release Reporting" under Section 313 (40 CFR 372).
EPA CERCLA/Superfund Reportable Spill Quantity	Not applicable.
EPA RCRA Hazardous Waste Classification	If product becomes a waste, it does NOT meet the criteria of a hazardous waste as defined by the US EPA.
California Proposition 65	The California Proposition 65 regulations apply to this product.
MA Right-to-Know Law	One or more components listed.
NJ Right-to-Know Law	One or more components listed.
PA Right-to-Know Law	One or more components listed.

Canadian Regulations

Canadian DSL Inventory	All components listed on inventory or are exempt.
WHMIS Hazard Class	B3 Combustible Liquids D1B Toxic Materials D2B Toxic Materials

16. OTHER INFORMATION

The following sections have been revised since the last issue of this MSDS
Not applicable

Additional Information

For additional information on the use of this product, contact your local Halliburton representative.

For questions about the Safety Data Sheet for this or other Halliburton products, contact Chemical Compliance at 1-580-251-4335.

Disclaimer Statement

*****END OF MSDS*****

HALLIBURTON

MATERIAL SAFETY DATA SHEET

Product Trade Name: **WellLock H1**

Revision Date: 12-Oct-2012

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product Trade Name:	WellLock H1
Synonyms:	None
Chemical Family:	Amine
Application:	Curing Agent
Manufacturer/Supplier	Halliburton Energy Services P.O. Box 1431 Duncan, Oklahoma 73536-0431 Emergency Telephone: (281) 575-5000
Prepared By	Chemical Compliance Telephone: 1-580-251-4335 e-mail: fdunexchem@halliburton.com

2. COMPOSITION/INFORMATION ON INGREDIENTS

Substances	CAS Number	PERCENT	ACGIH TLV-TWA	OSHA PEL-TWA
Diethyltoluenediamine	68479-98-1	60 - 100%	Not applicable	Not applicable

3. HAZARDS IDENTIFICATION

Hazard Overview	May be absorbed through the skin. May cause allergic skin reaction. May be harmful if swallowed. May cause severe eye irritation. May cause skin irritation.

4. FIRST AID MEASURES

Inhalation	If inhaled, remove to fresh air. If not breathing give artificial respiration, preferably mouth-to-mouth. If breathing is difficult give oxygen. Get medical attention.
Skin	Remove contaminated clothing and launder before reuse. In case of contact, immediately flush skin with plenty of soap and water for at least 15 minutes. Get medical attention. Destroy or properly dispose of contaminated shoes.
Eyes	In case of contact, or suspected contact, immediately flush eyes with plenty of water for at least 15 minutes and get medical attention immediately after flushing.
Ingestion	If swallowed, induce vomiting immediately by giving two glasses of water and sticking fingers down throat; never give anything to an unconscious person. Get medical attention.
Notes to Physician	Not Applicable

5. FIRE FIGHTING MEASURES

Flash Point/Range (F):	> 275
Flash Point/Range (C):	> 135
Flash Point Method:	Not Determined
Autoignition Temperature (F):	Not Determined
Autoignition Temperature (C):	Not Determined
Flammability Limits in Air - Lower (%):	Not Determined
Flammability Limits in Air - Upper (%):	Not Determined

Fire Extinguishing Media	Water fog, carbon dioxide, foam, dry chemical. Use water spray to cool fire exposed surfaces.
Special Exposure Hazards	Product will not burn unless preheated. Decomposition in fire may produce toxic gases.
Special Protective Equipment for Fire-Fighters	Full protective clothing and approved self-contained breathing apparatus required for fire fighting personnel.
NFPA Ratings:	Health 2, Flammability 1, Reactivity 0
HMIS Ratings:	Health 2, Flammability 1, Physical Hazard 1 , PPE: D

6. ACCIDENTAL RELEASE MEASURES

Personal Precautionary Measures	Use appropriate protective equipment.
Environmental Precautionary Measures	Prevent from entering sewers, waterways, or low areas.
Procedure for Cleaning / Absorption	Isolate spill and stop leak where safe. Contain spill with sand or other inert materials.

7. HANDLING AND STORAGE

Handling Precautions	Avoid contact with eyes, skin, or clothing. Wash hands after use. Avoid breathing vapors.
Storage Information	Store in a cool well ventilated area. Keep from excessive heat. Keep container closed when not in use. Store away from oxidizers.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering Controls	Use in a well ventilated area. Local exhaust ventilation should be used in areas without good cross ventilation.
Respiratory Protection	If engineering controls and work practices cannot keep exposure below occupational exposure limits or if exposure is unknown, wear a NIOSH certified, European Standard EN 149, or equivalent respirator when using this product. Selection of and instruction on using all personal protective equipment, including respirators, should be performed by an Industrial Hygienist or other qualified professional. Not normally needed. But if significant exposures are possible then the following respirator is recommended: Organic vapor/acid gas respirator with a dust/mist filter.
Hand Protection	Neoprene gloves. Nitrile gloves.
Skin Protection	Butyl coated apron or clothing.
Eye Protection	Chemical goggles; also wear a face shield if splashing hazard exists.

Other Precautions	Eyewash fountains and safety showers must be easily accessible.

9. PHYSICAL AND CHEMICAL PROPERTIES

Physical State:	Liquid
Color:	Clear
Odor:	Amine
pH:	Not Determined
Specific Gravity @ 20 C (Water=1):	1.02
Density @ 20 C (lbs./gallon):	8.50
Bulk Density @ 20 C (lbs/ft3):	Not Determined
Boiling Point/Range (F):	586
Boiling Point/Range (C):	307
Freezing Point/Range (F):	Not Determined
Freezing Point/Range (C):	Not Determined
Vapor Pressure @ 20 C (mmHg):	0.97 @ 126C/259F
Vapor Density (Air=1):	5.2
Percent Volatiles:	Not Determined
Evaporation Rate (Butyl Acetate=1):	Not Determined
Solubility in Water (g/100ml):	Partially soluble
Solubility in Solvents (g/100ml):	Not Determined
VOCs (lbs./gallon):	Not Determined
Viscosity, Dynamic @ 20 C (centipoise):	Not Determined
Viscosity, Kinematic @ 20 C (centistokes):	Not Determined
Partition Coefficient/n-Octanol/Water:	Not Determined
Molecular Weight (g/mole):	Not Determined

10. STABILITY AND REACTIVITY

Stability Data:	Stable
Hazardous Polymerization:	Will Not Occur
Conditions to Avoid	Keep away from heat, sparks and flame.
Incompatibility (Materials to Avoid)	Strong oxidizers. Strong acids. Reducing agents. Violent, explosive reaction with sulfur trioxide, decaborane, silver perchlorate, triethenyl aluminum, and hydrogen in presence of nickel catalyst at temperatures above 200 C.
Hazardous Decomposition Products	Oxides of nitrogen. Carbon monoxide and carbon dioxide.
Additional Guidelines	Not Applicable

11. TOXICOLOGICAL INFORMATION

Principle Route of Exposure	Eye or skin contact, inhalation.
Inhalation	May cause respiratory irritation.
Skin Contact	May cause skin irritation. May be absorbed through the skin and contribute to the symptoms listed under ingestion. May cause an allergic skin reaction.
Eye Contact	May cause severe eye irritation.
Ingestion	Harmful if swallowed.
Aggravated Medical Conditions	Diseases of the pancreas. Eye ailments. Skin disorders.

Chronic Effects/Carcinogenicity	A two year feeding study in rats showed DETDA caused effects in the pancreas, liver, thyroid, and eyes. An increase in the number of tumors in the liver and thyroid of male rats and in the liver and possibly mammary gland of female rats was found.
Other Information	None known.

Toxicity Tests

Oral Toxicity:	Not determined
Dermal Toxicity:	Not determined
Inhalation Toxicity:	Not determined
Primary Irritation Effect:	Not determined
Carcinogenicity	Not determined
Genotoxicity:	Not determined
Reproductive / Developmental Toxicity:	Not determined

12. ECOLOGICAL INFORMATION

Mobility (Water/Soil/Air)	Not determined
Persistence/Degradability	Not determined
Bio-accumulation	Not determined

Ecotoxicological Information

Acute Fish Toxicity:	May be highly toxic to aquatic life.
Acute Crustaceans Toxicity:	Not determined
Acute Algae Toxicity:	Not determined
Chemical Fate Information	Not determined
Other Information	Not applicable

13. DISPOSAL CONSIDERATIONS

Disposal Method	Disposal should be made in accordance with federal, state, and local regulations.
Contaminated Packaging	Follow all applicable national or local regulations.

14. TRANSPORT INFORMATION

Land Transportation

DOT

UN2810,Toxic Liquid, Organic, N.O.S.(Contains Diethyltoluenediamine), 6.1, III
NAERG 153

Canadian TDG
Toxic Liquid, Organic, N.O.S.(Contains Diethyltoluenediamine), 6.1, UN2810, III

ADR

UN2810,Toxic Liquid, Organic, N.O.S.(Contains Diethyltoluenediamine), 6.1, III

Air Transportation

ICAO/IATA

UN2810,Toxic Liquid, Organic, N.O.S., 6.1, III
(Contains Diethyltoluenediamine)

Sea Transportation

IMDG

UN2810,Toxic Liquid, Organic, N.O.S.(Contains Diethyltoluenediamine), 6.1, III
EmS F-A, S-A

Other Transportation Information

Labels:	Keep Away From Food

15. REGULATORY INFORMATION

US Regulations

US TSCA Inventory	All components listed on inventory or are exempt.
EPA SARA Title III Extremely Hazardous Substances	Not applicable
EPA SARA (311,312) Hazard Class	Acute Health Hazard Chronic Health Hazard
EPA SARA (313) Chemicals	This product does not contain a toxic chemical for routine annual "Toxic Chemical Release Reporting" under Section 313 (40 CFR 372).
EPA CERCLA/Superfund Reportable Spill Quantity	Not applicable.
EPA RCRA Hazardous Waste Classification	If product becomes a waste, it does NOT meet the criteria of a hazardous waste as defined by the US EPA.
California Proposition 65	All components listed do not apply to the California Proposition 65 Regulation.
MA Right-to-Know Law	Does not apply.
NJ Right-to-Know Law	Does not apply.
PA Right-to-Know Law	Does not apply.

Canadian Regulations

Canadian DSL Inventory	All components listed on inventory or are exempt.
WHMIS Hazard Class	D2B Toxic Materials

16. OTHER INFORMATION

The following sections have been revised since the last issue of this MSDS
Not applicable

Additional Information	For additional information on the use of this product, contact your local Halliburton representative. For questions about the Material Safety Data Sheet for this or other Halliburton products, contact Chemical Compliance at 1-580-251-4335.
Disclaimer Statement	This information is furnished without warranty, expressed or implied, as to accuracy or completeness. The information is obtained from various sources including the manufacturer and other third party sources. The information may not be valid under all conditions nor if this material is used in combination with other materials or in any process. Final determination of suitability of any material is the sole responsibility of the user.

*****END OF MSDS*****

MATERIAL SAFETY DATA SHEET

Product Trade Name: **MICROSAND**

Revision Date: 04-Jan-2011

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product Trade Name:	MICROSAND
Synonyms:	None
Chemical Family:	Sand
Application:	Additive
Manufacturer/Supplier	Halliburton Energy Services P.O. Box 1431 Duncan, Oklahoma 73536-0431 Emergency Telephone: (281) 575-5000
Prepared By	Chemical Compliance Telephone: 1-580-251-4335 e-mail: fdunexchem@halliburton.com

2. COMPOSITION/INFORMATION ON INGREDIENTS

Substances	CAS Number	PERCENT	ACGIH TLV-TWA	OSHA PEL-TWA
Crystalline silica, quartz	14808-60-7	60 - 100%	0.025 mg/m^3	10 mg/m^3 %SiO2 + 2

More restrictive exposure limits may be enforced by some states, agencies, or other authorities.

3. HAZARDS IDENTIFICATION

Hazard Overview

CAUTION! - ACUTE HEALTH HAZARD
May cause eye and respiratory irritation.

DANGER! - CHRONIC HEALTH HAZARD
Breathing crystalline silica can cause lung disease, including silicosis and lung cancer. Crystalline silica has also been associated with scleroderma and kidney disease.

This product contains quartz, cristobalite, and/or tridymite which may become airborne without a visible cloud. Avoid breathing dust. Avoid creating dusty conditions. Use only with adequate ventilation to keep exposures below recommended exposure limits. Wear a NIOSH certified, European Standard EN 149, or equivalent respirator when using this product. Review the Material Safety Data Sheet (MSDS) for this product, which has been provided to your employer.

4. FIRST AID MEASURES

Inhalation If inhaled, remove from area to fresh air. Get medical attention if respiratory irritation develops or if breathing becomes difficult.

Skin	Wash with soap and water.
Eyes	In case of contact, immediately flush eyes with plenty of water for at least 15 minutes and get medical attention if irritation persists.
Ingestion	Under normal conditions, first aid procedures are not required.
Notes to Physician	Not Applicable

5. FIRE FIGHTING MEASURES

Flash Point/Range (F):	Not Determined
Flash Point/Range (C):	Not Determined
Flash Point Method:	Not Determined
Autoignition Temperature (F):	Not Determined
Autoignition Temperature (C):	Not Determined
Flammability Limits in Air - Lower (%):	Not Determined
Flammability Limits in Air - Upper (%):	Not Determined

Fire Extinguishing Media	None - does not burn.
Special Exposure Hazards	Not applicable.
Special Protective Equipment for Fire-Fighters	Not applicable.
NFPA Ratings:	Health 0, Flammability 0, Reactivity 0
HMIS Ratings:	Health 0*, Flammability 0, Reactivity 0

6. ACCIDENTAL RELEASE MEASURES

Personal Precautionary Measures	Use appropriate protective equipment. Avoid creating and breathing dust.
Environmental Precautionary Measures	None known.
Procedure for Cleaning / Absorption	Collect using dustless method and hold for appropriate disposal. Consider possible toxic or fire hazards associated with contaminating substances and use appropriate methods for collection, storage and disposal.

7. HANDLING AND STORAGE

Handling Precautions	This product contains quartz, cristobalite, and/or tridymite which may become airborne without a visible cloud. Avoid breathing dust. Avoid creating dusty conditions. Use only with adequate ventilation to keep exposure below recommended exposure limits. Wear a NIOSH certified, European Standard En 149, or equivalent respirator when using this product. Material is slippery when wet.
Storage Information	Store in a cool, dry location. Use good housekeeping in storage and work areas to prevent accumulation of dust. Close container when not in use. Product has a shelf life of 36 months.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering Controls	Use approved industrial ventilation and local exhaust as required to maintain exposures below applicable exposure limits listed in Section 2.

Respiratory Protection	Wear a NIOSH certified, European Standard EN 149, or equivalent respirator when using this product.
Hand Protection	Normal work gloves.
Skin Protection	Wear clothing appropriate for the work environment. Dusty clothing should be laundered before reuse. Use precautionary measures to avoid creating dust when removing or laundering clothing.
Eye Protection	Wear safety glasses or goggles to protect against exposure.
Other Precautions	None known.

9. PHYSICAL AND CHEMICAL PROPERTIES

Physical State:	Solid
Color:	White to tan
Odor:	Odorless
pH:	Not Determined
Specific Gravity @ 20 C (Water=1):	2.65
Density @ 20 C (lbs./gallon):	Not Determined
Bulk Density @ 20 C (lbs/ft3):	38
Boiling Point/Range (F):	Not Determined
Boiling Point/Range (C):	Not Determined
Freezing Point/Range (F):	Not Determined
Freezing Point/Range (C):	Not Determined
Vapor Pressure @ 20 C (mmHg):	Not Determined
Vapor Density (Air=1):	Not Determined
Percent Volatiles:	Not Determined
Evaporation Rate (Butyl Acetate=1):	Not Determined
Solubility in Water (g/100ml):	Insoluble
Solubility in Solvents (g/100ml):	Not Determined
VOCs (lbs./gallon):	Not Determined
Viscosity, Dynamic @ 20 C (centipoise):	Not Determined
Viscosity, Kinematic @ 20 C (centistrokes):	Not Determined
Partition Coefficient/n-Octanol/Water:	Not Determined
Molecular Weight (g/mole):	60.9

10. STABILITY AND REACTIVITY

Stability Data:	Stable
Hazardous Polymerization:	Will Not Occur
Conditions to Avoid	None known.
Incompatibility (Materials to Avoid)	Hydrofluoric acid.
Hazardous Decomposition Products	Amorphous silica may transform at elevated temperatures to tridymite (870 C) or cristobalite (1470 C).
Additional Guidelines	Not Applicable

11. TOXICOLOGICAL INFORMATION

Principle Route of Exposure	Eye or skin contact, inhalation.

Inhalation

Inhaled crystalline silica in the form of quartz or cristobalite from occupational sources is carcinogenic to humans (IARC, Group 1). There is sufficient evidence in experimental animals for the carcinogenicity of tridymite (IARC, Group 2A).

Breathing silica dust may cause irritation of the nose, throat, and respiratory passages. Breathing silica dust may not cause noticeable injury or illness even though permanent lung damage may be occurring. Inhalation of dust may also have serious chronic health effects (See "Chronic Effects/Carcinogenicity" subsection below).

Skin Contact

None known.

Eye Contact

May cause mechanical irritation to eye.

Ingestion

None known

Aggravated Medical Conditions

Individuals with respiratory disease, including but not limited to asthma and bronchitis, or subject to eye irritation, should not be exposed to quartz dust.

Chronic Effects/Carcinogenicity

Silicosis: Excessive inhalation of respirable crystalline silica dust may cause a progressive, disabling, and sometimes-fatal lung disease called silicosis. Symptoms include cough, shortness of breath, wheezing, non-specific chest illness, and reduced pulmonary function. This disease is exacerbated by smoking. Individuals with silicosis are predisposed to develop tuberculosis.

Cancer Status: The International Agency for Research on Cancer (IARC) has determined that crystalline silica inhaled in the form of quartz or cristobalite from occupational sources can cause lung cancer in humans (Group 1 - carcinogenic to humans) and has determined that there is sufficient evidence in experimental animals for the carcinogenicity of tridymite (Group 2A - possible carcinogen to humans). Refer to IARC Monograph 68, Silica, Some Silicates and Organic Fibres (June 1997) in conjunction with the use of these minerals. The National Toxicology Program classifies respirable crystalline silica as "Known to be a human carcinogen". Refer to the 9th Report on Carcinogens (2000). The American Conference of Governmental Industrial Hygienists (ACGIH) classifies crystalline silica, quartz, as a suspected human carcinogen (A2).

There is some evidence that breathing respirable crystalline silica or the disease silicosis is associated with an increased incidence of significant disease endpoints such as scleroderma (an immune system disorder manifested by scarring of the lungs, skin, and other internal organs) and kidney disease.

Other Information

For further information consult "Adverse Effects of Crystalline Silica Exposure" published by the American Thoracic Society Medical Section of the American Lung Association, American Journal of Respiratory and Critical Care Medicine, Volume 155, pages 761-768 (1997).

Toxicity Tests

Oral Toxicity:	Not determined
Dermal Toxicity:	Not determined
Inhalation Toxicity:	Not determined
Primary Irritation Effect:	Not determined
Carcinogenicity	Refer to IARC Monograph 68, Silica, Some Silicates and Organic Fibres (June 1997).

Genotoxicity:	Not determined
Reproductive / Developmental Toxicity:	Not determined

12. ECOLOGICAL INFORMATION

Mobility (Water/Soil/Air)	Not determined
Persistence/Degradability	Not applicable
Bio-accumulation	Not determined

Ecotoxicological Information

Acute Fish Toxicity:	Not determined
Acute Crustaceans Toxicity:	Not determined
Acute Algae Toxicity:	Not determined

Chemical Fate Information	Not determined
Other Information	Not applicable

13. DISPOSAL CONSIDERATIONS

Disposal Method	Bury in a licensed landfill according to federal, state, and local regulations.
Contaminated Packaging	Follow all applicable national or local regulations.

14. TRANSPORT INFORMATION

Land Transportation

DOT
Not restricted

Canadian TDG
Not restricted

ADR
Not restricted

Air Transportation

ICAO/IATA
Not restricted

Sea Transportation

IMDG
Not restricted

Other Transportation Information

Labels:	None

15. REGULATORY INFORMATION

US Regulations

US TSCA Inventory	All components listed on inventory or are exempt.
EPA SARA Title III Extremely Hazardous Substances	Not applicable
EPA SARA (311,312) Hazard Class	Acute Health Hazard Chronic Health Hazard
EPA SARA (313) Chemicals	This product does not contain a toxic chemical for routine annual "Toxic Chemical Release Reporting" under Section 313 (40 CFR 372).
EPA CERCLA/Superfund Reportable Spill Quantity	Not applicable.
EPA RCRA Hazardous Waste Classification	If product becomes a waste, it does NOT meet the criteria of a hazardous waste as defined by the US EPA.
California Proposition 65	The California Proposition 65 regulations apply to this product.
MA Right-to-Know Law	One or more components listed.
NJ Right-to-Know Law	One or more components listed.
PA Right-to-Know Law	One or more components listed.

Canadian Regulations

Canadian DSL Inventory	All components listed on inventory or are exempt.
WHMIS Hazard Class	D2A Very Toxic Materials Crystalline silica

16. OTHER INFORMATION

The following sections have been revised since the last issue of this MSDS
Not applicable

Additional Information	For additional information on the use of this product, contact your local Halliburton representative. For questions about the Material Safety Data Sheet for this or other Halliburton products, contact Chemical Compliance at 1-580-251-4335.
Disclaimer Statement	This information is furnished without warranty, expressed or implied, as to accuracy or completeness. The information is obtained from various sources including the manufacturer and other third party sources. The information may not be valid under all conditions nor if this material is used in combination with other materials or in any process. Final determination of suitability of any material is the sole responsibility of the user.

*****END OF MSDS*****

Enclosure #4

DuPont Position on IARC Classification of Titanium Dioxide

DuPont Titanium Technologies
Chestnut Run Plaza 728, Rm. 2204
974 Centre Road
P. O. Box 2915
Wilmington, DE 19805
FAX (1) (302) 999-5159

February 1, 2013

Titanium Dioxide and IARC Classification

In February 2006, the International Agency for Research on Cancer (IARC), an arm of the World Health Organization, changed the classification of TiO_2 to possibly carcinogenic to humans (2B). This Monograph was published in January 2011 as Monograph 93. It can be accessed at http://monographs.iarc.fr/ENG/Monographs/vol93/index.php .

Attached you will find a web-link from the Titanium Dioxide Manufacturers Association (TDMA), a European Chemical Industry Council (CEFIC) sector group, of which the DuPont Titanium Technologies business is a member, explaining the background and implications of this listing:
http://www.tdma.info/fileadmin/pdf/about_tio2/TDMA%20TDSC%20IARC%20Statement%2019%2007%2011.final.pdf

We have updated our Material Safety Data Sheets (MSDS) to reflect this change. Our updated MSDSs can be found at:
http://www2.dupont.com/Titanium_Technologies/en_US/msds/index.html
Click on the country/language you want, click on "go", and then click on the appropriate grade you purchase.

Ti-Pure® products may not be directly added to food, pharmaceuticals, cosmetics, or cigarette papers/filters for tobacco products. It is DuPont's policy that Ti-Pure® products may not be used in medical applications involving implantation in the human body.

If you should have any questions, please call me at (1) (302) 999-5259. Thank you for your interest in Ti-Pure® products.

Sincerely,

Michael J. Kletter

Michael J. Kletter, Ph.D.
Product Stewardship and
Regulatory Program Manager
michael.j.kletter-1@usa.dupont.com

TDMA

Titanium Dioxide Manufacturers Association
(A sector group of cefic)

Avenue E. Van Nieuwenhuyse, 4 box 1
B-1160 Brussels (Belgium)
Phone: +32 2 676 73 27

TiO_2

Titanium Dioxide Stewardship Council

2200 Pennsylvania Avenue, N.W. ◆ Suite 100W ◆
Washington, D.C. 20037 ◆ (202) 557-3800 tel. ◆
(202) 557-3836 fax

Titanium Dioxide Product Safety Statement on Inhalation Toxicology

Introduction

In February 2006 the International Agency for Research on Cancer (IARC) reclassified titanium dioxide (TiO_2). The final Monograph was published in January 2011. This document explains the significance of this reclassification and the position of TDMA.

Background/History

In 1989 IARC classified TiO2 as Group 3: ('not classifiable for human carcinogenicity'). TiO2 is usually used in toxicological studies as an inert comparator or control. However, three long term studies were specifically carried out on TiO2, at exposure concentrations far above those experienced in any workplace. After two years exposure at this „overload“ concentration, lung tumors were found in rats.

The TiO_2 industry commissioned a TiO_2 inhalation study in mice, rats and hamsters and two epidemiology studies in 15 TiO_2 plants in Europe and North America.

Main findings of these studies

The epidemiology studies did not demonstrate an increased risk of lung cancer as a result of occupational exposure to TiO_2.

The inhalation study clearly demonstrated that rats exhibited a different response to high TiO_2 dust concentrations compared with mice and hamsters.

The unique response developed by rats significantly adds to the evidence that the observed effects are not relevant to humans. It was the dust overload that fundamentally caused the problem in rats. There is no evidence that titanium dioxide *itself* has toxic properties that would lead to cancer, nor that it presents a carcinogenic risk to humans at exposures experienced in the workplace.

Actions in 2006

In February 2006 IARC carried out a review which resulted in the classification for TiO2 being changed from Group 3 to Group 2B, i.e. from: *'not classifiable for human carcinogenicity'* to: *'possible human carcinogen'*.

This reclassification was based *entirely* on the long term animal studies. The epidemiology studies led the panel to conclude there was *'insufficient evidence of carcinogenicity in humans'*. For the animal studies, the conclusion was: *'sufficient evidence of carcinogenicity in experimental animals'*.

Enclosure #5

Titanium Dioxide section of "IARC Monograph on the Evaluation of Carcinogenic Risk in Humans: Carbon Black, Titanium Dioxide and Talc."

World Health Organization. Volume 93; pages 193-276. January, 2011.

TITANIUM DIOXIDE

Titanium dioxide was considered by a previous Working Group in October 1988 (IARC, 1989). Since that time, new data have become available, and these have been included in the present monograph and taken into consideration in the evaluation.

1. Exposure Data

1.1 Chemical and physical data

1.1.1 *Nomenclature*

Chem. Abstr. Services Reg. No.: 13463–67–7, titanium dioxide; 1317–70–0, anatase titanium dioxide; 1317–80–2, rutile titanium dioxide
Chem. Abstr. Name: Titanium dioxide
IUPAC Systematic Name: Titanium dioxide
Synonyms: CI: 77891; dioxotitanium oxide; E 171; NCI-CO4240; Pigment White 6; titania; titanic oxide; titanium oxide; titanium (IV) oxide; titanium peroxide

1.1.2 *Molecular formula and relative molecular mass*

TiO_2 Relative molecular mass: 79.90

1.1.3 *Chemical and physical properties of the pure substance*

Description: Fine white powder (Windholz, 1983)
Crystal structure
Four naturally occurring titanium dioxide polymorphs exist: rutile, anatase, brookite and titanium dioxide(B) (Banfield & Veblen, 1992). Anatase and rutile are tetragonal, brookite is orthorhombic and titanium dioxide(B) is monoclinic. In all four polymorphs, titanium is coordinated octahedrally by oxygen, but the position of the octahedra differs between polymorphs. The structure of rutile is the most dense and its unit cell is the smallest. Anatase has four formula units per unit cell with a = 0.379 nm and c = 0.951 nm; rutile has two with a = 0.459 nm and c = 0.296 nm; brookite has eight with a = 0.917 nm, b = 0.546 nm and c = 0.514 nm; and titanium

dioxide(B) has eight with a = 1.216 nm, b = 0.374 nm, c = 0.651 nm and β = 107.29° (Banfield & Veblen, 1992). Only the structures of rutile (titanium dioxide-rutile) and anatase (titanium dioxide-anatase) are reported in commercial products.

Density of ideal minerals: Anatase, 3.79 g/cm^3; rutile, 4.13 g/cm^3; brookite, 3.99 g/cm^3; and titanium dioxide(B), 3.64 g/cm^3 (Banfield & Veblen, 1992)

Refractive index: Anatase, 2.561, 2.488; rutile, 2.605–2.616, 2.890–2.903; and brookite, 2.583, 2.700 (Phillips & Griffen, 1981)

Hardness on Moh's scale: Anatase, 5.5–6; rutile, 6–6.5; and brookite, 5.5–6 (Harben & Kuzvart, 1996)

Solubility: Soluble in sulfuric acid and alkalis; insoluble in water (Weast, 1985)

Spectroscopy: X-Ray diffraction patterns for anatase and rutile are available from the International Center for Diffraction Data (2005), which maintains the powder diffraction file.

Chemical composition: Natural rutile, anatase and brookite contain impurities of up to ≈2% that include iron, chromium, vanadium, aluminium, niobium, tantal, hafnium and zirconium (Heaney & Banfield, 1993) and account for slight variations in density, colour and indices of refraction. Since most commercial titanium dioxide is manufactured from natural material by dissolution of the parent mineral and reprecipitation as fine particles with the structure of anatase or rutile (referred to as titanium dioxide-anatase or titanium dioxide-rutile), most but not all of these chemical impurities are generally removed.

Other characteristics: Titanium dioxide is an ultraviolet (UV)-activated catalyst, and organic polymers that are in contact with it degrade under UV radiation. Anatase is 10 times more active than rutile and responds to slightly different wavelengths (Braun, 1997).

1.1.4 *Technical products and impurities*

Trade names for titanium dioxide include Aeroxide, A-Fil Cream, Atlas white titanium dioxide, Austiox, Bayertitan, Calcotone White T, Comet, Cosmetic White C47–5175, Cosmetic White C47–9623, C-Weiss 7, Flamenco, Hitox, Hombitan, Hombitec, Horse Head A-410, Horse Head A-420, Horse Head R-710, Kemira, KH 360, Kronos titanium dioxide, Levnox White RKB, Pretiox, Rayox, Runa RH20, Rutile, Rutil RC, Rutiox, Tichlor, Tiofine, TiO2 Hombitan, Tiona T.D., Tioxide, Tipaque, Ti-Pure, Ti-Select, Titafrance, Titan, Titania, Titandioxid, Titanium White, Titanox, Titanox 2010, Trioxide(s), Tronox, Tytanpolr, Unitane products (various), UV-Titan, 1700 White and Zopaque.

(a) Particle size

Titanium dioxide particles are referred to as primary, aggregates or agglomerates. Primary particles are single crystals that are bound by crystal planes. Aggregates are sintered primary particles that are connected by crystal faces. Agglomerates are multiple primary particles and aggregates that are held together by van der Waal's forces.

Scattering of light by titanium dioxide is maximized in particles that are 0.2–0.3 μm in diameter, and most commercial products that are used as pigments have modal primary particle sizes within this range. The range of ultrasonically dispersed primary particles and aggregates is narrow, and generally ranges from <0.1 to 0.5 μm (Braun, 1997; Linak *et al.*, 2002; Swiler, 2005). A recent study showed that commercial pigments contain almost no particles <0.1 μm. This range may not apply to bulk material, which contains aggregates that are not broken down during industrial use (Braun, 1997).

Non-pigmentary titanium dioxide is composed of either uncoated manufactured titanium dioxide (both titanium dioxide-anatase and titanium dioxide-rutile) or ground natural rutile. In general, these products contain coarser particles than pigmentary titanium dioxide (Linak *et al.*, 2002).

Ultrafine titanium dioxide particles (nanoparticles) range in size from 1 to 150 nm (Linak *et al.*, 2002), with a modal primary particle size of 10–50 nm. They are generated by sol-gel synthesis and the wide variation in their morphology and size is controlled by the pH of the gel.

Primary particles generally form aggregates and agglomerates and are not normally found as discrete particles. In commercial products, the particle size of pigmentary and ultrafine material is approximately equal because of aggregation and agglomeration (American Chemistry Council, 2005).

Titanium dioxide has also been produced as engineered nanomaterials, which may be equidimensional crystals or sheets and are composed of either titanium dioxide-rutile or titanium dioxide-anatase. A tubular structure has been produced from scrolling layers of titanium dioxide-anatase, which results in fibres with an outer diameter of about 6 nm and an inner tube of about 3 nm (Barnard *et al.*, 2005). Non-scrolled nanofibres have also been produced from titanium dioxide-anatase and titanium dioxide(B) with diameters of 20–100 nm and lengths of 10–100 μm (Pavasupree *et al.*, 2005).

(b) Types of titanium-dioxide pigment

According to the American Society for Testing and Materials (ASTM, 1988) D476–84 standard, four types of titanium dioxide pigment exist (Schurr, 1981; Fisher & Egerton, 2001):

Type I (94% titanium dioxide min.) is a titanium dioxide-anatase pigment that chalks [forms a layer of loose pigment powder on the surface of weathered paint film] freely and is used in white interior and exterior house paints.

Type II (92% titanium dioxide min.) is a titanium dioxide-rutile pigment that has a medium resistance to chalking and is used in varying amounts in all types of interior paints, enamels and lacquers.

Type III (80% titanium dioxide min.) is also a titanium dioxide-rutile pigment that has a medium resistance to chalking and is used principally in alkyd and emulsion flat-wall paints.

Type IV (80% titanium dioxide min.) is another titanium dioxide-rutile pigment that has a high resistance to chalking; it is used in exterior paints and has excellent durability and gloss retention.

The Japanese grading system, the JIS K5116–1973, specifies four grades of titanium dioxide-rutile, three of which contain at least 92% titanium dioxide and the fourth contains a minimum of 82%. The type of coating in each grade is also specified (Fisher & Egerton, 2001).

(c) Extenders, impurities and coatings

Titanium dioxide extenders were used in commercial pigments in the past, but are not generally employed now. Calcium sulfate (Braun, 1997) and barium sulfate (Fisher & Egerton, 2001) were commonly used during the early years of production, and other materials that may have been used as extenders for white pigment include calcium carbonate, alumina, silica and kaolin (Linak *et al.*, 2002).

Titanium dioxide-anatase pigments may contain titanium dioxide-rutile. Before coating, titanium dioxide-anatase produced by the sulfate process contains both phosphorous and sulfate that are concentrated at the particle surface. In addition, uncoated titanium dioxide-anatase pigments retain about 0.3% niobium pentoxide and 0.3% phosphorus pentoxide from the ore and up to 0.2% alumina that is added during manufacture (Braun, 1997).

Prior to coating, titanium dioxide-rutile pigments that are produced by chlorination contain about 1% alumina, which is concentrated at the surface of the particles (Braun 1997), but not titanium dioxide-anatase.

With the exception of non-pigmentary titanium dioxide such as ground rutile and titanium dioxide-anatase that are used as food additives, all commercially produced titanium dioxide is coated by a variety of oxides and oxyhydrates by aqueous precipitation techniques. These coatings improve dispersibility, dispersion stability, opacity, durability and gloss. They form a barrier between the titanium dioxide and organic substances, such as those found in paints, and prevent contact catalysis. In some cases, organic or silicone treatments may be added after initial coating. Titanium dioxide-rutile pigments generally contain 1–15% of coatings and titanium dioxide-anatase pigments contain 1–5% of coatings. The most common coatings are composed of oxyhydrates and oxides of aluminium and silicone. Oxides and oxyhydrates of zirconium, tin, zinc, phosphorous, cerium and boron are also used (Linak *et al.*, 2002). Table 1.1 (American Chemistry Council, 2005) gives the types of coating that are used in decreasing order of importance.

The thickness of these coatings is variable but may be only a few atom layers. They are generally coherent over the surface of the titanium dioxide particle (American Chemistry Council, 2005), but some titanium oxide and titanium hydroxide may also be present on the surfaces (Braun, 1997). The thinness of the coatings precludes most techniques of structural analysis and their atomic structure therefore remains largely unknown (Braun, 1997). The composition (but not necessarily the atomic structure) of the alumina coatings are γ-AlOOH (bohemite), α-AlOOH (diaspor) and γ-Al(OH)$_3$ (hydrargillite). The silica coatings may be fluffy, and consist of polymerized silicic acid or a dense, true shell of glass. Ultrafine titanium dioxide is also coated; examples of coatings are given in Table 1.2.

Coating with alumina and silica can more than double the surface area (Braun, 1997). The surface area of untreated pigment ranges from 8 to 10 m^2/g, while treated pigment surface areas generally span 8–19 m^2/g and matt-finish pigments (that have high levels of alumina) can extend up to 35 m^2/g. Surface areas of the ultrafine products are in the range of 35–100 m^2/g (American Chemistry Council, 2005).

Titanium dioxide-coated surface and pigments are hydrophilic; those coated with silicones are not used as pigment because they are hydrophobic.

Table 1.1. Types of coating used for common grades of titanium dioxide pigment (normally titanium dioxide-rutile)

Surface treatment type	Composition, range (wt %)	Application
Alumina/TMP	Al_2O_3, 1.0–5.5 Total carbon, <0.3	Paint/coatings
Alumina/zirconia/TMP	Al_2O_3, 1.0–5.0 ZrO_2, 0.3–1.0 Total carbon, <0.3	Paint/coatings
Alumina/silica/siloxane	Al_2O_3, 1–6 SiO_2, 0.3–3 Total carbon, <0.3	Plastics
Alumina/silica/TMP	Al_2O_3, 1.0–6.0 SiO_2, 0.5–13.0 Total carbon, <0.3	Paint/coatings/plastics
Alumina/TME	Al_2O_3, 1.0–3.5 Total carbon, <0.3	Paint/coatings
Alumina/zirconia/TME	Al_2O_3, 1.0–5.0 ZrO_2, 0.3–1.0 Total carbon, <0.3	Paint/coatings
Alumina/silica/TME	Al_2O_3, 1.5–5.0 SiO_2, 1.5–3.5 Total carbon, <0.3	Paint/coatings
Alumina/silica/silane	Al_2O_3, 1.0–6.0 SiO_2, 0.3–3 Total carbon, <0.3	Plastics

From American Chemistry Council (2005)
TME, trimethylol ethane; TMP, trimethylol propane; wt, weight

Table 1.2. Relative proportion[a] of the production of common grades of ultrafine titanium dioxide used in sunscreens with different types of coating

Organic	Inorganic				
	None	Silica 5–25%	Alumina 1–25%	Silica 1–10% + alumina 5–15%	Sodium meta-phosphate 1–5%
None	2	4	3	4	1
Stearate 5–15% as carbon			16		
Butyl glycol dicaprylate 60% + stearate 5%		1			
Methicone max. 11%		1	1		
Dimethicone 1–10%			2	4	
Dimethicone/siloxane 2% as SiO_2			2		
Dimethicone/methicone copolymer 1–10%	2	2		4	
Simethicone 5% (as SiO_2) + water 13%	2				
Trimethylsiloxysilicone 1–10%				4	
Polyvinyl-pyrrolidone max. 3%			1		
Alkyl silane 2.7–3.7% as carbon	1				
Glycerin max. 1%			1		
Alginate 1–5%				1	

From American Chemistry Council (2005)
[a] 16=high, 1=low

1.1.5 *Analysis*

Exposure to particulates in occupational environments is generally determined gravimetrically. The behaviour of titanium dioxide in air and its deposition in the respiratory tract upon inhalation are important factors in human exposure, and are determined by the aerodynamic diameter of the particles. The aerodynamic diameter can be measured by impactors and is dependent upon the geometric diameter, [material] density and shape [factor] of the aggregates. Most commonly, the size distribution of airborne particles is expressed as the mass median aerodynamic diameter (MMAD) and the geometric standard deviation. Several dust fractions are often identified, namely, ‘total’ dust, inhalable dust and respirable dust.

Inhalable dust approximates the fraction of airborne material that enters the nose and mouth during breathing and is therefore available for deposition anywhere in the respiratory tract (International Standards Organization, 1995; Health and Safety Executive, 2000). The inhalable fraction depends on the prevailing movement of air around the exposed person and whether breathing is by the nose or mouth. It is, however, possible to define target specifications for sampling instruments that approximate the inhalable fraction and these are provided by the International Standards Organization (1995). In the United Kingdom, the standard sampling devices for measuring inhalable dust are the multiorifice sampler and the Institute of Medicine (IOM) sampler (Health and Safety Executive, 2000).

Respirable dust approximates the fraction of airborne material that penetrates the gas-exchange region of the lung. The respirable fraction varies between individuals; however, it is possible to define a target specification for sampling instruments that approximates the respirable fraction for an average person (International Standards Organization, 1995). Respirable dust is generally collected using a cyclone preselector (Health and Safety Executive, 2000).

The term 'total' dust refers to total particulates that are represented (in North America at least) by the material that is collected by a closed-face three-piece plastic sampling cassette that holds a 37-mm filter (Eller & Cassinelli, 1994). The term 'total' dust is not equivalent to all airborne dust; in fact, measurements of inhalable dust by the IOM sampling head are 1.0–2.5 times higher than 'total' dust levels using a closed-face 37-mm filter cassette, depending on the aerodynamic diameter of the particles (Werner *et al.*, 1996).

Analysis of different types of coatings is accomplished by transmission electron microscopy equipped with energy-dispersive X-ray spectroscopy.

1.2 Production and use

1.2.1 *Production*

The manufacture of pure titanium white for use as a pigment (anatase form) was first reported in 1923 in France. The growth of the production and use of titanium white pigments began in the early 1930s and continued until recently, but the rate has now decreased. In 2004, worldwide production was estimated at 4.4 million tonnes (Swiler, 2005).

(a) Sources

Titanium dioxide pigments are manufactured from a variety of ores that contain ilmenite ($FeTiO_3$), rutile, anatase and leucoxene ($TiO_2.xFeO.yH_2O$), which are mined from deposits located throughout the world. Titanium may also be recovered from slag produced during iron smelting and from synthetic rutile produced from ilmenite.

Large deposits of titanium dioxide occur in association with igneous rocks and as heavy mineral deposits in unconsolidated sands (Garnar & Stanaway, 1994; Chang, 2002). Major igneous deposits are found in Brazil, Canada, Norway, the Russian Federation and the Ukraine (Chang, 2002).

Important heavy mineral sands are found along the eastern and western coasts of Australia, the eastern coast of South Africa, the southeastern coast of the USA, the west coast of South Island, New Zealand, the eastern coast of China, the northeastern coast of Sri Lanka, at various locations along the southern coast of India, in coastal Malaysia and in alluvial deposits in Sierra Leone and China (Chang, 2002).

Anatase, brookite and titanium dioxide(B) are common minor constituents in soils and sediments, particularly those derived from titanium-rich rocks. Rutile is a common accessory mineral in a wide variety of crustal and mantle-derived rocks and in sediment and sedimentary rocks (Heaney & Banfield, 1993).

Ilmenite is found in beach sand in existing or fossil coastlines and is an important raw material in titanium dioxide production. Surface processes alter the ilmenite in these deposits to produce submicroscopic mixtures of minerals that include anatase, rutile and amorphous phases. Mixtures that contain as much as 90% titanium dioxide are referred to as leucoxene. Leucoxene is recovered from some deposits and treated separately. However, the quantities produced are small in comparison with those of ilmenite. The concentrates obtained from ilmenite sand, which are depleted of iron, are generally richer in titanium dioxide than those from the massive deposits. Other elements in these concentrates include magnesium, manganese and vanadium that are present in the ilmenite, and aluminum, calcium, chromium and silicon (Kischkewitz *et al.*, 2002).

The second most commonly available ore is the buff-coloured mineral rutile, which contains about 95% titanium dioxide with smaller amounts of iron and other impurities. The rutile contained in primary rocks cannot be extracted. Only sands in which rutile is accompanied by zircon and/or ilmenite and other heavy minerals can be used as raw materials. Rutile sands are mostly found in Australia, Sierra Leone and South Africa. The importance of mineral rutile to the titanium dioxide industry is waning. In the 1970s, it accounted for 20% of the feedstock, but now accounts for less than 10% due to diminishing reserves (Kischkewitz *et al.*, 2002; Linak & Inoguchi, 2005).

Anatase, like rutile, is a modification of titanium dioxide. The largest reserves of this mineral are found in carboniferous intrusions in Brazil. Techniques for preparation of the ore produce concentrates that contain 80% titanium dioxide, and further concentration to 90% titanium dioxide is possible by treatment with hydrochloric acid (Kischkewitz *et al.*, 2002).

(b) Processing

There are five stages in the manufacture of pigmentary titanium dioxide. First, titanium dioxide ore is converted to either aqueous titanyl sulfate solution or anhydrous titanium tetrachloride. These intermediates are then converted to crystalline, size-specific pigmentary particles of titanium dioxide-rutile or titanium dioxide-anatase. The pigment is coated, in some cases involving a grinding step, and then filtered, washed and dried. Finally, the pigment agglomerates may be ground to reduce their size without breaking the primary titanium dioxide particles (Braun, 1997).

Most ores are concentrated or otherwise processed to increase the titanium dioxide content before they are suitable as a raw material for pigment production. Impurities such as iron and alkaline earth elements colour the ores from buff to black and must be removed to obtain a clean white titanium dioxide pigment (Kischkewitz *et al.*, 2002; Linak & Inoguchi, 2005).

Direct use of ilmenites has decreased due to their high iron content. A digestion process is employed to produce iron sulfate heptahydrate from ilmenite. When iron sulfate is not required as a product, metallurgical recovery of iron from iron-rich ilmenites and production of a titanium-rich slag are increasingly being used (Kischkewitz *et al.*, 2002; Linak & Inoguchi, 2005).

Titanium dioxide pigment is produced from titanium mineral concentrates by either the chloride process or the sulfate process. In the sulfate process, ilmenite or titanium slag is reacted with sulfuric acid. Titanium hydroxide is then precipitated by hydrolysis, filtered and calcined. In the chloride process, rutile is converted to titanium tetrachloride by chlorination in the presence of petroleum coke. The titanium tetrachloride is oxidized by air or oxygen at about 1000°C, and the resulting titanium dioxide is calcined to remove residual chlorine and any hydrochloric acid that may have formed in the reaction. Aluminium chloride is added to the titanium tetrachloride to ensure that virtually all the titanium is oxidized into the rutile crystal structure. Although either process may be used to produce pigment, the decision to use one process instead of the other is based on numerous factors, including the availability of raw materials, freight and waste disposal costs. In finishing operations, the crude form of the pigment is milled to produce a controlled distribution of particle size and the surface is treated or coated to improve its functional behaviour in different media. Typical surface treatments include alumina, organic compounds (e.g. polyols, esters, siloxanes, silanes) and silica (Kischkewitz *et al.*, 2002; Gambogi, 2003).

Each producer of titanium dioxide has its own purity requirements and hence places different values on certain physical properties. For example, Japanese producers tend to prefer ilmenite which has a higher ferrous oxide content but a lower titanium dioxide content than the ores generally favoured by European producers (Kischkewitz *et al.*, 2002; Linak & Inoguchi, 2005).

(c) Capacity, production and consumption

In 2004, world production of titanium mineral concentrates had increased to 5.2 million tonnes from 4.6 million tonnes in 2000. Approximately 95% is used as feedstock for titanium dioxide and the remainder is used in titanium metal alloys. In 2004, the leading supplier of titanium feedstock was South Africa (25%), followed by Australia (21%), Canada (14%), China (8%), the Ukraine (7%) and Norway (7%) (Linak & Inoguchi, 2005).

Approximately 60 plant sites worldwide (outside of China) produce titanium dioxide, with an average annual capacity of 60 000 tonnes. Table 1.3 presents world titanium dioxide capacity by region and process for 1993, 1998, 2002 and 2005 (Linak & Inoguchi, 2005).

In recent years, most increases in capacity have been through the development of small plants in China and other less developed regions. Until recently, global capacity had been growing faster than demand, resulting in oversupply and erosion of prices. In real terms, prices have been decreasing on average by about 1% per year for the past 20 years (Linak & Inoguchi, 2005).

For environmental, economic and qualitative reasons, chloride process plants continue to be favoured over sulfate plants in industrialized countries, particularly for new production facilities. Operators of sulfate process plants have had to invest in waste acid recycling facilities to extend operating lives. In addition, the production of rutile pigment from the chloride process has increased (Linak & Inoguchi, 2005).

Titanium dioxide is used in more than 170 countries. The major exporting regions are North America and Australia, and most of the countries in the rest of the world are net importers. Table 1.4 presents world supply and demand for titanium dioxide in 1997, 2001 and 2004 (Linak & Inoguchi, 2005).

1.2.2 *Use*

Titanium dioxide is valued for its opacifying strength (commonly called hiding power) and brightness. Other important features of titanium dioxide pigments are excellent resistance to chemical attack, good thermal stability and resistance to UV degradation. Rutile pigment is more resistant to UV light than anatase, and is preferred for paints, plastics, especially those exposed to outdoor conditions, and inks. Anatase pigment has a bluer tone than the rutile type, is less abrasive and is used mainly in indoor paints and in paper, ceramics, rubber and fibres manufacture. Both rutile and anatase pigments can be made more resistant to photodegradation by coating the pigment particles, which also improves their dispersibility, dispersion stability, opacity and gloss. Usually alumina, silica, zirconia or a combination of these is used; silica is most effective in retarding the photoactivity of the pigment, while alumina is most effective in enhancing dispersibility and binder compatability. Generally, rutile pigments contain 1–15% coating and anatase pigments contain 1–5%. The higher levels of coating are given to pigments that are typically used for applications such as flat (low-gloss) paints (Linak & Inoguchi, 2005).

The major consumer industries for titanium dioxide pigments are mature sectors in high-resource countries where they are used for surface coatings, paper and paperboard and plastics. Therefore, consumption of titanium dioxide tends to parallel general economic trends. Paint and coating applications have the largest global use, and plastics and paper account for most of the remainder. World consumption of titanium dioxide by end-use in 2001 was: coatings, 55%; plastics and rubber, 24%; paper, 12%; printing inks, 3%; and other, 6%; that in 2005 was: coatings, 58%; plastics and rubber, 23%; paper, 11%;

Table 1.3. World capacity for titanium dioxide (thousand tonnes, gross weight)

Region	1993			1998			2002			2005		
	S	C	Total	S	C	Total	S	C	Total	S	C	Total
North America	202	1288	1488	178	1436	1614	134	1656	1790	80	1717	1797
Central and South America	55	0	55	60	0	60	60	0	60	96	0	96
Western Europe	875	317	1192	913	405	1318	925	472	1397	862	547	1409
Central and eastern Europe	195	0	195	203	0	203	217	0	217	234	0	234
Africa and Middle East	35	50	85	40	80	119	40	100	140	25	100	125
Japan	270	50	319	272	52	324	259	68	327	240	68	308
China	–	–	–	–	–	–	258	408	666	658	15	673
Oceania and other Asia	224	114	338	291	184	475	–	–	–	141	404	545
Total	1856	1819	3672	1957	2157	4113	1893	2704	4597	2336	2857	5187

From Linak & Inoguchi (2005)
C, chloride process; S, sulfate process

Table 1.4. World production and consumption of titanium dioxide (thousand tonnes, gross weight)

Region	1997		2001		2004	
	P	C	P	C	P	C
North America						
Canada	75	105	68	90	76	104
Mexico	102	37	124	65	124	64
USA	1340	1129	1340	1100	1511	1162
Central and South America						
Brazil	79	108	78	111	80	124
Other	0	60	0	60	0	85
Western Europe	1113	1099	1150	1100	1254	1183
Central and eastern Europe	136	125	155	155	155	155
Africa and Middle East						
Saudi Arabia	50	10	55	10	90	30
Other Middle East	0	60	0	65	0	120
South Africa	30	25	30	20	20	28
Other Africa	0	15	0	35	0	45
Japan	241	269	257	246	253	238
Oceania and other Asia						
Australia	160	40	181	66	200	40
China	102	170	147	256	350	540
India and Pakistan	50	70	44	77	52	82
Indonesia	–	–	–	–	0	49
Malaysia	–	–	50	28	50	15
Philippines	–	–	–	–	0	33
Republic of Korea	35	100	42	118	40	120
Singapore	–	–	41	16	45	30
Southeast Asia	77	145	–	–	–	–
Taiwan (China)	68	71	123	66	120	66
Thailand	–	–	–	–	0	71
Other	–	–	0	108	0	29
Total	3658	3638	3885	3792	4420	4423

C, consumption; P, production
From Linak & Inoguchi (2005)

and other, 8% (Linak & Inoguchi, 2005). Some other uses of titanium dioxide are in catalysts, ceramics, coated fabrics and textiles, floor coverings and roofing granules (Gambogi, 2005; Swiler, 2005).

Despite their lower price, anatase-grade pigments account for only 10% of total global production. About two-thirds of the total anatase supply is used in markets where quality is less important, such as paper, low-priced emulsion paints, or tiles and enamels. Only one-third of the anatase is used in applications for which its specific properties are highly valued, such as when a bluish tint is desired in some plastics. Anatase is also used because of its photocatalytic properties; total global demand for its use as an active material for the removal of nitrogen oxide compounds from waste gases of coal-fired power plants and for the cleaning of exhaust gases of diesel engines is 15 000 tonnes per year (Linak & Inoguchi, 2005; Swiler, 2005).

Traditionally, the industry has produced a wide variety of grades of titanium dioxide that are tailored for specific applications. In recent years, producers have introduced so-called 'multipurpose products' to try to reduce the number of grades needed in an effort to increase operating efficiency. For example, in the paint market, titanium dioxide manufacturers propose a universal product that is acceptable for use in flat (low-gloss) and enamel (high-gloss) coatings (Linak & Inoguchi, 2005).

Some products with coarse particle sizes are obtained at an intermediate step (before coating with inorganic oxides) in the manufacture of pigmentary titanium dioxide. Manufacturers propose a 'buff' titanium dioxide that is made by grinding rutile ore to yield a product with a 95% titanium dioxide content that can be used as a partial replacement for white titanium dioxide in formulations that are tinted with other colour pigments. Total estimated global production of pigment by this process is about 10 000 tonnes per year (Kischkewitz *et al.*, 2002; Linak & Inoguchi, 2005).

Ultrafine grades of titanium dioxide (particle size, 1–150 nm), which transmit visible light but scatter UV radiation, are used as UV blockers in sunscreens and plastics, catalysts and colour pigment precursors and in electroceramics (Kischkewitz *et al.*, 2002; Linak & Inoguchi, 2005).

Relatively small quantities of titanium dioxide are used for non-pigmentary purposes. The estimated global market is 110 000 tonnes per year, and the largest user sectors are enamels and ceramics (25–30%), glass and glass ceramics (25–30%), electroceramics (10–15%), catalysts and catalyst supports (10–15%) and welding fluxes (10–15%) (Kischkewitz *et al.*, 2002; Linak & Inoguchi, 2005).

1.3 Occurrence and exposure

1.3.1 *Natural occurrence*

Titanium is the ninth most abundant element in the world, it is five times less abundant than iron but 100 times more abundant than copper. The chemical composition of titanium dioxide is described in detail in Section 1.1.3 and its sources in Section 1.2.1(*a*).

1.3.2 *Occupational exposure*

On the basis of a National Occupational Exposure Survey, conducted in the USA between 1981 and 1983, the National Institute for Occupational Safety and Health (NIOSH, 1983) estimated that 2.7 million workers (2.2 million men and 0.5 million women) were potentially exposed to titanium dioxide. [This estimate is based on a survey of companies and did not involve measurements of actual exposure; for many workers, very low levels and/or incidental exposures to titanium dioxide may be incurred.]

No estimate of the number of workers currently exposed to titanium dioxide was available to the Working Group.

(*a*) *Manufacture of titanium dioxide*

The highest levels of exposure within a titanium dioxide manufacturing plant are generally observed in the milling and packing areas (Fryzek *et al.*, 2003). In these areas, titanium dioxide is finely processed by micronizers, and dust from the bags used for shipment may be dispersed through the air during bagging by the packers. Lower, but consistent, exposure to titanium dioxide may be incurred by treatment operators, who are involved in the addition of special coatings to and treatments of titanium dioxide before the product is finally milled and packed. Although maintenance mechanics are not exposed to titanium dioxide on a daily basis, they may experience short periods of heavy exposure during routine maintenance and repair activities associated with precipitation of titanium dioxide and subsequent processes or post-oxidation steps. Minimal exposure to titanium dioxide is incurred by workers who are involved in the initial processing and refinement of the product. In addition, general labourers or helpers, laboratory workers who work mainly in the laboratories to monitor the product and workers who handle raw ore also have minimal exposure to titanium dioxide.

Fryzek *et al.* (2003) reported results from 914 personal full-shift or near full-shift air samples for 'total' titanium dioxide that were obtained from four plants between 1976 and 2000 (Table 1.5). Eighteen of these samples appeared to the authors to be unrealistically high and were limited to 50 mg/m^3. The highest exposures were observed for packers, micronizers and workers involved in shovelling spilled titanium dioxide into bags (n=686; mean, 6.0 mg/m^3). Exposure levels decreased over time from a mean of 13.7 mg/m^3 (n=21) in 1976–80 to 7.9 mg/m^3 (n=87) in 1981–85, 6.4 mg/m^3 (n=210) in 1986–90, 5.3 mg/m^3 (n=239) in 1991–95 and 3.1 mg/m^3 (n=357) in 1996–2000.

In seven titanium dioxide manufacturing plants in Europe, Boffetta *et al.* (2003) reported results from 1348 personal exposure measurements of titanium dioxide dust that were predominantly collected during routine measurement programmes. The results related to inhalable, respirable and 'total' dust measurements, which were converted to respirable dust levels using several conversion factors. To convert 'total' to inhalable dust, a conversion factor of 1.2 was used, based on a study by Kenny *et al.* (1997). A factor of 0.3 was chosen to convert inhalable titanium dioxide dust measurements to respirable measurements, based on results from a study in the European carbon black manufacturing industry (Gardiner *et al.*, 1992). Table 1.6 summarizes the results for these standardized levels of respirable titanium dioxide for the packing areas in these plants. The highest levels were observed in Factory 10, where the geometric mean (GM) respirable dust levels ranged from 7.99 mg/m^3 between 1970 and 1974 to approximately 1.3–2.2 mg/m^3 between 1980 and 1999. The authors mentioned that one of the possible reasons for the relatively high exposure levels in Factory 10 may reflect the conversion factors used rather than actual differences in exposure, and care should be taken when interpreting the differences in exposure between the factories.

Although not reported in the study by Boffetta *et al.* (2003, 2004), results from other areas in the titanium dioxide plants were also obtained. Table 1.7 includes results from inhalable and 'total' dust measurements that have been converted to respirable dust levels, and should therefore be interpreted with some care. Highest levels of exposure to respirable dust were found in the drying and milling (GM range, 0.19–2.12 mg/m^3) and packing (GM, 0.48–2.11 mg/m^3) areas, although high exposure levels were also observed for maintenance workers (GM, 0.62–2.24 mg/m^3), handymen (GM, 4.02 mg/m^3) and cleaners (GM, 5.02 mg/m^3). Exposure levels appear to have declined between 1970 and 2000, due to the implementation of control measures such as local exhaust ventilation, increased automation and isolation or segregation of personnel (Sleeuwenhoek, 2005).

To enable a quantitative exposure–response analysis, exposure reconstruction was undertaken for each occupational title at each plant for different time periods (Boffetta *et al.*, 2003, 2004) using a method developed by Cherrie *et al.* (1996). The yearly estimated exposure to titanium dioxide dust by factory between 1950 and 1999 varied between 0.1 and 1.0 mg/m^3 (Boffetta *et al.*, 2004). However, very high exposure levels were estimated (>7 mg/m^3) in several factories either for cleaning jobs during the end of the production process or for jobs that involved recycling of titanium dioxide dust. Jobs with the highest estimated exposure to titanium dioxide were recycling/blending, sweeper, cleaner, packing, drying, warehouseman and fitter/mechanic (Boffetta *et al.*, 2003). The authors observed a decreasing trend in exposure, particularly in factories with the highest estimated exposures during the early production period. Although the highest exposure levels in the factory were in the order of 1.0 mg/m^3, average levels ranged up to 5.0 mg/m^3 for individual occupational titles (Boffetta *et al.*, 2004).

Somewhat higher exposure levels were found in earlier studies. Reported concentrations of total dust ranged from 10 to 400 mg/m^3 during the grinding of titanium dioxide pigment, but documentation of these levels was not provided (Elo *et al.*, 1972). Long-term exposures to titanium dioxide dust in a titanium pigment production factory occasionally exceeded 10 mg/m^3, and exposures greater than 10 mg/m^3 were common during the repair of production machinery (Rode *et al.*, 1981).

Table 1.5. Personal 'total' exposure to titanium dioxide in four titanium dioxide manufacturing plants in the USA by job category (1976–2000)

Job category	No.	Mean (mg/m^3)	SD	Median (mg/m^3)	GM (mg/m^3)
Packers, micronizers and addbacks	686	6.2	9.4	3.0	2.7
Ore handlers	21	1.1	1.1	0.9	0.6
Maintenance mechanics	59	2.5	6.9	0.7	0.7
Dry and wet treatment	117	2.0	7.6	0.3	0.4
Other exposed jobs	31	0.6	0.9	0.4	0.4

Adapted from Fryzek *et al.* (2003)
GM, geometric mean; No., number of samples; SD, standard deviation

Table 1.6. Exposure to titanium dioxide in packing areas in titanium dioxide manufacturing plants in Europe

Factory	Year	No. of measurements	GM (mg/m^3)	Interquartile range	Range
1	1995–99	55	1.33	0.46–3.31	0.10–19.86
	2000–02	9	0.68	0.20–2.74	0.13–4.17
3	1990–94	1	0.25	–	–
	1995–99	61	0.88	0.50–1.90	0.04–7.74
	2000–02	6	0.69	0.27–1.75	0.27–3.83
6	1990–94	6	1.24	0.61–2.47	0.47–5.14
	1995–99	13	2.51	1.63–4.31	0.72–9.72
8	1995–99	11	0.77	0.48–0.96	0.32–6.16
9	1985–89	12	1.57	0.96–2.44	0.72–4.64
	1990–94	16	2.00	1.44–3.08	0.64–3.39
	1995–99	18	1.31	0.80–1.99	0.40–4.24
10	1970–74	10	7.99	3.64–16.64	2.34–79.20
	1975–79	20	2.49	1.64–3.53	1.01–6.41
	1980–84	22	2.16	1.25–3.88	0.63–10.91
	1985–89	18	1.31	0.94–1.93	0.68–5.04
	1990–94	19	1.34	0.94–2.23	0.32–5.29
	1995–99	6	2.11	1.60–3.28	0.47–3.96
15	1985–89	76	0.47	0.31–0.70	0.02–3.54
	1990–94	92	0.45	0.29–0.66	0.06–4.94
	1995–99	37	0.63	0.32–1.57	0.04–4.89

Adapted from Boffetta *et al.* (2003)
GM, geometric mean

Table 1.7. Measurements of respirable dust (mg/m^3) from the white end[a] of the titanium dioxide manufacturing process in Europe (1970–2000)

Area	Plant	No.	GM	Interquartile range	Range
Moore filtration	1	8	0.11	0.06–0.54	<0.01–0.94
	8	8	0.28	0.16–0.64	0.08–0.80
Calcination	10	28	0.78	0.36–1.25	0.18–4.79
	15	4	1.01	0.40–3.18	0.39–3.68
Raymond mills and conveying	9	29	1.20	0.88–1.72	0.25–3.84
Surface treatment	1	59	0.66	0.29–1.31	0.05–17.30
	15	5	0.10	0.04–0.37	0.04–0.57
Drying and milling	3	30	0.44	0.12–1.62	0.02–10.80
	8	2	0.71	–	0.48–1.04
	9	46	2.12	1.40–3.82	0.49–7.76
	10	135	1.37	0.86–2.09	0.32–20.66
	15	6	0.19	0.08–0.89	0.02–2.35
Packing	1	64	1.21	0.45–2.97	0.10–19.86
	3	68	0.84	0.46–1.72	0.04–7.74
	6	19	2.01	1.25–4.26	0.47–9.72
	8	11	0.77	0.48–0.96	0.32–6.16
	9	46	1.59	0.96–2.57	0.04–4.64
	10	95	2.11	1.12–3.42	0.32–79.20
	15	205	0.48	0.30–0.70	0.02–4.94
Warehouse	3	38	0.29	0.15–0.53	0.04–4.89
	10	6	1.96	1.32–2.84	1.08–3.28
Forklift truck driver	15	12	0.45	0.24–0.97	0.14–2.14
Loader	15	13	0.29	0.15–0.35	0.10–4.98
Maintenance	1	32	0.62	0.14–1.59	0.04–9.07
	3	28	0.97	0.33–2.79	0.04–18.86
	10	47	2.24	1.30–3.38	0.54–10.19
White end	8	5	1.36	0.60–3.32	0.32–3.44
Handyman	10	44	4.02	2.54–7.35	0.72–20.16
Cleaner	10	9	5.02	3.40–8.71	1.15–9.68

Adapted from Sleeuwenhoek (2005)

GM, geometric mean

[a] White end, TiO_2 precipitation and all subsequent processes

(b) Particle concentration

Wake *et al.* (2002) reported the results of measurements taken with a P-trak, Portacount or scanning mobility particle sizer in a titanium dioxide manufacturing plant in the United Kingdom. The particle number concentrations in the bagging area ranged from 4.2×10^3 particles/cm^3 to 16.6×10^3 particles/cm^3 compared with 9.7–58.4 × 10^3 particles/cm^3 outside the plant on the same day, which indicated that exposure to ultrafine particles (not in conglomerates) is relatively low. [The report does not specify what method was used to count the airborne titanium dioxide particles or what size particles were included in these measurements.]

Various other exposure concentrations have been reported in the manufacture of titanium dioxide, such as ore and other dusts, sulfuric acid, sulfur dioxide, welding fumes, hydrochloric acid and asbestos.

(c) User industries

Titanium dioxide is used in various industries (see Section 1.2.2) and exposure may occur before and during the addition of titanium dioxide to matrices such as paints, coatings, plastics, rubber, ink and foodstuffs. The potential for exposure is greatly reduced in other parts of the process. Very little information is available on exposure to titanium dioxide in various user industries.

In the pulp, paper and paper product industry, Kauppinen *et al.* (2002) estimated that 70% of stock preparation departments had an exposure prevalence greater than 5% (i.e. more than 5% of the workforce was exposed); this proportion was 73% for on-machine coating of paper. The median level of exposure in these departments was assessed to be between 1.5 and 10 mg/m^3.

No significant exposure to primary particles of titanium dioxide is thought to occur during the use of products in which titanium dioxide is bound to other materials, such as in paints.

1.3.3 *Environmental exposure*

No information was available to the Working Group on environmental exposure to titanium dioxide.

1.4 Regulations and guidelines

Occupational exposure regulations and guidelines in several countries are presented in Table 1.8.

Current occupational exposure limits for titanium dioxide in the USA are based on the airborne mass fractions of either respirable or 'total' dust fractions, and may be the same for titanium dioxide and particles that are not otherwise regulated or classified, with limits ranging from 1.5 mg/m^3 for respirable dust excluding ultrafine particles (Federal Republic

Table 1.8 Occupational exposure standards and guidelines for titanium dioxide

Country or region	Concentration (mg/m^3)	Interpretation
Austria	6	TWA – ACC
Belgium	10	TWA – ACC
China	8 (T)	TWA
	10 (T)	STEL
	0 (T)	Ceiling
Canada		
Alberta	10 (T)	TWA
British Columbia	3 (R)	TWA
	10 (T)	TWA
	20 (T)	STEL
Ontario	10 (T)	TWA
Quebec	10 (T)	TWA; containing no asbestos and < 1% crystalline silica
Czech Republic	10	TWA – ACC
Denmark	6 (as Ti)	TWA
Finland	10	TWA
France	10	TWA
Germany	1.5[a] (R)	MAK (see also aerosol allowable concentrations)
Greece	10	TWA – ACGIH (from ACC)
Hong Kong	3 (R)	TWA
	10 (T)	TWA
Ireland	4 (R)	TWA
	10 (I)	TWA
Italy	10	TWA – ACGIH (from ACC)
Mexico	10	TWA
	20	STEL
Netherlands	10 (I)	TWA – ACC
	5 (R)	TWA – ACC
New Zealand	10 (I)	TWA; containing no asbestos and <1% free silica
Norway	5	TWA
Poland	10 (I)	TWA; containing no asbestos and <2% free crystalline silica
Portugal	10	TWA – ACGIH (from ACC)
South Africa	5 (R)	TWA
	10 (I)	TWA
Spain	10	TWA
Sweden	5 (T)	TWA
Switzerland	3	TWA
United Kingdom	4 (R)	TWA
USA		
ACGIH (TLV)	10 (A4)	TWA
NIOSH (REL)	(Ca)	lowest feasible concentration
OSHA (PEL)	15 (T)	TWA

From Direktoratet for Arbeidstilsynet (2002); SUVA (2003); American Chemistry Council (2003); ACGIH Worldwide (2005); Deutsche Forschungsgemeinschaft (2005); Health and Safety Executive (2005); INRS (2005); Työsuojelusäädöksiä (2005)

A4, not classifiable as a human carcinogen; ACC, American Chemistry Council; ACGIH, American Conference of Government Industrial Hygienists; Ca, potential occupational carcinogen; I, inhalable dust; MAK, maximum concentration at the workplace; NIOSH, National Institute of Occupational Health; OSHA, Occupational Safety and Health Administration; PEL, permissible exposure limit; R, respirable dust; REL, recommended exposure level; STEL, short-term exposure limit; T, total dust; TLV, threshold limit value; TWA, 8-h time-weighted average

[a] Excluding ultrafine or aggregates of ultrafine

of Germany maximum concentration value in the workplace) to 15 mg/m^3 for total dust (Occupational Safety and Health Administration, 2002). The National Institute for Occupational Safety and Health (NIOSH, 2005) currently has no recommended exposure limit for titanium dioxide in the USA and classifies it as a potential occupational carcinogen. [The Working Group is aware that the National Institute for Occupational Health is considering recommending exposure limits of 1.5 mg/m^3 for fine titanium dioxide and 0.1 mg/m^3 for ultrafine titanium dioxide as time-weighted average concentrations for up to 10 hour per day during a 40-hour work week. This recommendation would remove the current classification of titanium dioxide as an occupational carcinogen.]

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2. Studies of Cancer in Humans

Studies on compounds related to titanium dioxide such as titanium tetrachloride or titanium metal dust (Garabrant *et al.*, 1987; Fayerweather *et al.*, 1992) are not included in this monograph.

2.1 Case report

Yamadori *et al.* (1986) reported a papillary adenocarcinoma of the lung and titanium dioxide-associated pneumoconiosis in a male titanium dioxide packer with 13 years of potential dust exposure and a 40-year history of tobacco smoking.

2.2 Cohort studies (Table 2.1)

Chen and Fayerweather (1988) conducted an industry-based epidemiological study and described mortality and cancer incidence among 1576 male employees who had been exposed to titanium dioxide for more than 1 year in two plants in the USA. Information on cancer incidence was obtained from the company cancer registry, which was started in 1956. Information on deaths among active and retired employees was obtained from the company mortality registry, which was started in 1957. Vital status was determined for about 94% of the cohort, and death certificates were available for about 94% of those known to have died. Observed numbers of incident cases of cancer were compared with expected numbers based on company rates, and the observed numbers of deaths were compared with both company rates and rates in the USA. Mortality from all cancers was lower than expected. For lung cancer, nine deaths were observed, with 17.3 expected on the basis of national rates (standardized mortality ratio (SMR), 0.52 [95% confidence interval (CI), 0.24–0.99]) and 15.3 expected on the basis of company rates (SMR, 0.59 [95% CI, 0.27–1.12]). There was a slight excess of incident cases of cancer (38 observed, 32.6 expected; SMR, 1.17 [95% CI, 0.83–1.60]) due mainly to 10 cases of tumours of the genitourinary system versus 6.3 expected (SMR, 1.59 [95% CI, 0.76–2.92]); eight cases of lung cancer were observed whereas 7.7 were expected (SMR, 1.04 [95% CI, 0.45–2.05]). No increase in mortality from other cancers was observed. [The Working Group noted that details of exposure to titanium dioxide and other factors were not described, that cancer mortality and specific cancer sites were not reported in detail, that incident cases of cancer only in actively employed persons were used for both observed and company reference rates, and that the numbers of incident cases were compared only with company rates.]

In a nested case–control study conducted in a cohort of workers from the oldest and largest of the two plants, no increased risk for lung cancer was found with estimated

Table 2.1. Industry-based studies of titanium dioxide and cancer

Reference, location	Study population	Exposure assessment	Exposure categories	No. of cases/ deaths	SMR (95% CI)	Adjustment for potential confounders comments
Chen & Fayerweather (1988); Fayerweather *et al.* (1992), USA	1576 male wage-grade employees in two titanium dioxide production plants who worked for ≥1 year before 1 January 1984; mortality follow-up from 1935 through to 1983; incident cases of cancer in 1956–85 from company insurance records	Committees were established at the plants to estimate exposure to titanium dioxide for all jobs; a cumulative exposure index, duration and time-weighted average were derived and used in the analysis.	Lung cancer	**Deaths**		Age, exposure to titanium tetrachloride, potassium titanate fibres, asbestos; unclear how the exposure history for controls in the nested case–control study was obtained; unclear if quantitative results from exposure monitoring or sampling were used; adjustment for smoking only made for case–control analyses.
				9	0.52 (0.24–0.99)	
				9	0.59 (0.27–1.12)	
				Cases		
				8	1.04 (0.45–2.05)	
				Cases (from case–control study)		
				16	0.6 (CI not reported)	
			Genito-urinary cancers	10/6.3	[1.59 (0.76–2.91)]	
Fryzek *et al.* (2003), USA	Retrospective mortality cohort study of 3832 male and 409 female workers employed for ≥6 months at four titanium dioxide production industries on or after 1 January 1960; follow-up until December 2000	Exposure levels to titanium dioxide assessed by industrial hygienists and based on job history	*All causes*	**Deaths**	**SMR**	Sex, age, race, time period, state where the plant was located; not adjusted for smoking; 35% of workers employed in jobs with high potential exposure to titanium dioxide (packers, micronizers, add-backs)
			All exposures	533	0.8 (0.8–0.9)	
			Packers, micronizers and Addbacks	112	0.7 (0.6–0.9)	
			Trachea, bronchus, lung cancer			
			All exposures	61	1.0 (0.8–1.3)	
			Packers, micronizers and Addbacks	11	1.0 (0.5–1.7)	
			Urinary cancer			
			All exposures	3	0.4 (0.1–1.3)	

Table 2.1 (contd)

Reference, location	Study population	Exposure assessment	Exposure categories	No. of cases/ deaths	SMR (95% CI)	Adjustment for potential confounders comments
Boffetta *et al.* (2004), Finland, France, Germany, Italy, Norway, United Kingdom	15 017 employees for at least 1 month in production of 11 European titanium dioxide industries (14 331 men); employment started from 1927–69 and ended 1995–2001; mortality follow-up 1950–72 until 1997–2001 (variable per country); 371 813 person–years.	Occupational hygienists reconstructed exposures for each occupational title; exposure estimates were linked with occupational history.	All causes/cancers	**Deaths**		Age/birth cohort, sex, calendar year; women were not included in most analyses (33 deaths only); national rates were used in comparisons.
				All causes		
				2619 men	0.87 [0.83–0.90]	
				33 women	0.58 (0.40–0.82)	
				All cancers		
				807 men	0.98 (0.91–1.05)	
				18 women	0.96 (0.58–1.54)	
				Lung cancer		
				307 men	1.23 (1.10–1.38)	
				1 woman	0.80 (0.02–4.09)	
			Exposure to respirable titanium dioxide dust (mg/m^3)–year			
			Lung cancer	*Men*		
			0–0.73	53	1.0 (reference)	
			0.73–3.43	53	1.19 (0.80–1.77)	
			3.44–13.19	52	1.03 (0.69–1.55)	
			≥13.20	53	0.89 (0.58–1.35)	
					(*p* for trend=0.5)	
			Kidney cancer			Results for kidney cancer were based on 13 cases among men.
			<4.0		0.45 (0.12–1.16)	
			4.0–13.9		1.15 (0.31–2.89)	
			≥14		1.18 (0.37–2.67)	
					(*p* for trend=0.09)	

CI, confidence interval; SMR, standardized mortality ratio exposure to either titanium dioxide or titanium tetrachloride (Fayerweather *et al.*, 1992). [The Working Group noted important methodological limitations of this study, such as a lack of detailed information on exposure assessment, duration of exposure and type of follow-up.]

Fryzek *et al.* (2003) conducted a multicentre study in the USA that included 5713 workers employed on or after 1 January, 1960 for at least 6 months at four titanium dioxide manufacturing plants. Among these, 1472 worked exclusively in administration or in other jobs that did not involve exposure to titanium dioxide. The remaining 4241 workers were followed up until 31 December 2000 (average follow-up, 21 years; standard deviation, 11 years). More workers were employed in chloride plants (53%) than in sulfate plants (40%) and 7% could not be categorized. Nearly 2400 records of air sampling measurements of sulfuric acid mist, sulfur dioxide, hydrogen sulfide, hydrogen chloride, chlorine, titanium tetrachloride and titanium dioxide were obtained from the four plants. Most were area samples and many were of short duration. Exposure assessment was conducted by industrial hygienists with expertise in historical exposure reconstruction. A combination of walk-through surveys, interviews with knowledgeable long-term employees and historical industrial hygiene measurements taken at the plants were used to assign exposure levels to study subjects based on their job history. Only the long-term area samples for total titanium dioxide dust were used. Exposure categories (defined by plant, job title and calendar years in the job) were created to examine mortality patterns for those jobs in which the potential for exposure to titanium dioxide was greatest. Exposure variables representing average exposure per year, years exposed and cumulative exposure were created for titanium dioxide and subjects were categorized into low, medium and high categories of exposure. A total of 914 full-shift or near full-shift personal samples for total titanium dioxide dust were used to estimate relative exposure concentrations between jobs over time (see Table 1.5). The number of expected deaths was based on mortality rates by sex, age, race, time period and the state in which the plant was located. Cox proportional hazard models that adjusted for the effects of age, sex, geographical area and date of first employment were used to estimate relative risks of exposure to titanium dioxide (i.e. average intensity, duration and cumulative exposure) in medium- or high-exposure groups versus the lowest exposure group. SMRs were calculated for all workers as well as separately by type of plant (sulfate and chloride). Information on vital status was found for 4194 of the 4241 (99%) workers in the study cohort. Of the 4241 workers (58% white, 90% male), 958 did not have adequate information on work history and were omitted from some plant analyses. Of the 533 deceased workers, information on cause of death was found for 511 (96%). Thirty-five per cent of the workforce had worked in one of the jobs with the highest potential exposure to titanium dioxide, i.e. packing, micronizing or internal recycling. Information on tobacco smoking was abstracted from medical records for 2503 workers across all four plants from 1960 onwards, but no individual adjustments were possible. It was stated that SMRs for women did not differ appreciably from those for men and only analyses for both sexes combined were presented. The SMR for all causes of death was significantly lower than expected (SMR, 0.8; 95% CI, 0.8–0.9); the SMR for all causes of death for sulfate plants was higher (SMR, 0.9; 95% CI, 0.8–1.0) than that for chloride plants (SMR, 0.6; 95% CI, 0.5–0.7). The number of lung cancers was close to that expected (SMR, 1.0; 95% CI, 0.8–1.3), with little variation by type of plant (sulfate plant: SMR, 1.1; 95% CI, 0.7–1.6; chloride plant: SMR, 0.9; 95% CI, 0.6–1.3). No significant increases were seen for any cause of death by type of plant, and no trends with exposure were observed. Workers with the highest exposure to titanium dioxide (packing, micronizing or internal recycling workers) had a similar pattern of mortality, i.e. significantly smaller number of deaths than that expected for all causes with no excess for lung cancer. No trend of increasing SMRs for malignant or non-malignant lung disease with increasing duration of employment was evident. Internal analyses showed that relative risks for mortality from all causes and mortality due to lung cancer and non-malignant respiratory disease decreased with increasing cumulative exposure. [This cohort was relatively young (about half were born after 1940) making the duration of exposure to titanium dioxide and the latency period for the development of lung cancer rather short. Moreover, the oldest company reports were not available for the authors to evaluate.]

In response to a letter by Beaumont *et al.* (2004), Fryzek *et al.* (2003) indicated no significant exposure–response relationships for mortality from lung cancer and cumulative exposure to titanium dioxide (i.e. ‘low’, ‘medium’ and ‘high’) with either a time-independent or a time-dependent exposure variable and a 15-year exposure lag (adjusted for age, sex, geographical area and date of first employment).

Boffetta *et al.* (2004) studied mortality from lung cancer among workers employed in 11 plants that produced titanium dioxide in six European countries (Finland, France, Germany, Italy, Norway and the United Kingdom). Overall, 27 522 titanium dioxide-exposed workers first employed between 1927 and 2001 were identified. Workers who were first employed after 1990, employed for less than 1 year in total or who worked in non-production jobs were excluded from analyses, which left a total of 15 017 workers (14 359 men and 686 women). Of the 11 plants, seven had only produced titanium dioxide using the sulfate process and two had only produced titanium dioxide using the chloride process. One plant operated both sulfate and chloride processes and the other plant that currently used the sulfate process had operated a chloride process for a short period. Follow-up for mortality was conducted in all countries and ranged from 27 years in Italy (1972–99) to 47 years in the United Kingdom (1954–2001). A total of 3.3% of cohort members were lost to follow-up and 0.7% had emigrated. The cause of death was unknown for 5.9% of deceased cohort members. Two occupational hygienists performed a comprehensive assessment of exposure, which was carried out at the level of occupational title for each plant for discrete time periods throughout the history of plant operations. Exposures to respirable titanium dioxide dust, sulfuric acid mist, hydrochloric acid, asbestos and welding fumes were assessed and indices of cumulative exposure were calculated by combining estimates across the entire occupational history of a worker. Exposure reconstruction was based on personal sample measurements that were mainly collected during the 1990s (see Section 1.3). Two factories had measurements from the late 1980s onwards and one factory had measurements from 1990 onwards. Information on tobacco smoking status was collected for 37.6% of workers included in the analyses. During the period of follow-up, 2619 male and 33 female deaths occurred. The SMR for all causes of death was significantly decreased in both genders: 0.87 [95% CI, 0.83–0.90] among men and 0.58 (95% CI, 0.40–0.82) among women. The country-specific SMR for all causes of death in men ranged from 0.81 in Finland to 0.97 in France. The number of deaths due to all malignant neoplasms was similar to that expected (SMR, 0.98; 95% CI, 0.91–1.05). The only cause of death with a statistically significant increased SMR was lung cancer (SMR, 1.23; 95% CI, 1.10–1.38), based on a fixed-effects statistical model. The SMRs varied from 0.76 (95% CI, 0.39–1.32) in Finland to 1.51 (95% CI, 1.26–1.79) in Germany. Because the heterogeneity between countries was of borderline significance (*p*-value=0.05), a random-effects model was also fitted and gave an SMR of 1.19 (95% CI, 0.96–1.48). There was no evidence of a significant difference in the SMRs for lung cancer according to job titles, or between the sulfate process (including no difference between the black and white ends) and the chloride process. Death rates from lung cancer did not increase with cumulative exposure to titanium dioxide dusts or with duration of employment in titanium dioxide manufacturing plants. In addition, many of the regions where the factories were located had a higher death rate from lung cancer than the national rate for their country, which implied that the SMR for lung cancer would have been lower if regional reference mortality had been used. The analysis of tobacco smoking was limited by the relatively small proportion of workers with known habits mainly during the recent period of follow-up but suggested that, for all countries other than France and the United Kingdom, titanium dioxide workers had a higher prevalence of smoking than the respective national populations. Mortality from lung cancer was not associated with exposure to sulfuric acid mist, asbestos or welding rod fumes in the factory workplace. A positive, non-significant dose–response relationship was suggested between estimated cumulative exposure to titanium dioxide dust and mortality from kidney cancer. No increase was found for this neoplasm in the SMR analysis: the SMRs for the three categories of estimated cumulative exposure to titanium dioxide dust were 0.45 (95% CI, 0.12–1.16), 1.15 (95% CI, 0.31–2.89) and 1.18 (95% CI, 0.37–2.67). Four deaths from pleural cancer were observed, one of which occurred in a worker with only 2 years of employment in the titanium dioxide production industry. Job information was totally lacking for one case and largely lacking for another; however, the remaining jobs in which these workers were employed did not obviously entail exposure to asbestos, although it should be noted that asbestosis was mentioned on the death certificate of one of them. Mortality from pleural cancer in this cohort did not seem to be increased compared with national rates. [Among the strengths of the European titanium dioxide study are the large size, the high follow-up rate and the detailed exposure assessment. The availability of data on tobacco smoking, although limited to slightly more than one-third of the cohort, provided some reassurance that tobacco smoking was unlikely to be a confounder. Besides the lack of adjustment for smoking, other limitations are possible exposure misclassification, which might have biased the results towards the null, the exclusion of part of the early experience of the cohort from the analysis, which reduces the power of the study to detect an association, and the relatively recent beginning of operation of some of the factories that resulted in a follow-up period that was too short to allow the detection of an increase in risk for lung cancer.]

2.3 **Community-based case–control studies** (Table 2.2)

Siemiatycki (1991) conducted a hypothesis-generating case–control study in Montréal, Canada, that has been described in detail in the monograph on carbon black. More than 4000 subjects were interviewed and included patients with 20 different types of cancer and a series of population controls. A panel of industrial hygienists reviewed each job history reported by study subjects and assessed exposure to 293 substances. Results on associations between titanium dioxide and several sites of cancer were reported. Some indications of excess risk were found in relation to squamous-cell lung cancer (odds ratio, 1.6; 90% CI, 0.9–3.0; 20 cases) and urinary bladder cancer (odds ratio, 1.7; 90% CI, 1.1–2.6; 28 cases). No excesses were observed for any exposure to titanium dioxide for all lung cancer combined (odds ratio, 1.0; 90% CI, 0.7–1.5; 38 cases), for kidney cancer (odds ratio, 1.1; 90% CI, 0.6–2.1; seven cases) or for cancer at several other sites other than the urinary bladder (odds ratio, 1.7; 90% CI, 1.1–2.6).

Subsequently, Boffetta *et al.* (2001) undertook a new in-depth analysis of the relationship between titanium dioxide and lung cancer in the Montréal study. They included 857 histologically confirmed cases of lung cancer diagnosed during 1979–85 among men aged 35–70 years and a group of controls comprising 533 randomly selected healthy residents and 533 cases of cancer of organs other than the lung. In preparation for the new analysis, the industrial hygienists reviewed and modified some of the attributions of exposure to titanium dioxide. The analysis also used a slightly different categorization for considering subjects as exposed to titanium dioxide. Exposure was classified as 'substantial' when it occurred for more than 5 years at a medium or high frequency and level. Most workers who were classified as exposed to titanium dioxide were painters and motor vehicle mechanics and repairers with painting experience; the highly exposed cases mixed raw materials for the manufacture of paints and plastics that contained titanium dioxide. [The Working Group noted that exposure to paints that contain titanium dioxide may not entail exposure to titanium dioxide particles.] Thirty-three cases and 43 controls were classified as having been exposed to titanium dioxide, for which the odds ratio was 0.9 (95% CI, 0.5–1.5). Results of unconditional logistic models were adjusted for age, socioeconomic status, ethnicity, respondent status (i.e. self or proxy), tobacco smoking, asbestos and exposure to benzo[*a*]pyrene. No trend was apparent according to the estimated frequency, level or duration of exposure for which the odds ratio was 1.0 (95% CI, 0.3–2.7) for medium or high exposure for at least 5 years. Few subjects were classified as exposed to titanium dioxide fumes or to other titanium compounds, but the risk for lung cancer was non-significantly increased for exposure to these agents. Results did not depend on the choice of control group and no significant

Table 2.2. Community-based case–control studies of titanium dioxide and cancer

Reference, study location, period	Characteristics of cases and controls	Exposure assessment	Exposure categories	Exposed cases	Odds ratio (90% CI)	Adjustment for potential confounders and comments
Siemiatycki (1991), Canada, 1979–86	Urinary bladder, lung, squamous-cell lung; 3730 histologically confirmed cases of 20 different cancer types diagnosed from September 1979 to June 1985 in men aged 35–70 years; 533 randomly selected healthy residents and 533 cancer controls not matched	Industrial hygienists/ chemists evaluated occupational histories to estimate exposure	*Occupational exposure*	*Urinary bladder cancer*		Age, family income, ethnicity, respondent (self/proxy), smoking, coffee consumption; hypothesis-generating study (293 exposures were evaluated); substantial exposure was defined as ≥10 years in the industry or occupation up to 5 years before onset
			Any	28	1.7 (1.1–2.6)	
			Substantial	3	4.5 (0.9–22.0)	
				Lung cancer		
			Any	38	1.0 (0.7–1.5)	
			Substantial	5	2.0 (0.6–7.4)	
				Squamous-cell lung cancer		
			Any	20	1.6 (0.9–3.0)	
			Substantial	2	1.3 (0.2–9.8)	
Boffetta *et al.* (2001), Canada	Lung cancer; 857 incident cases from 1979 to 1985; men aged 35–70 years; 533 randomly selected healthy residents and 533 cancer controls not matched	Industrial hygienists based on occupational histories collected by Siemiatycki (1991)			**Odds ratio (95%CI)**	Age, family income, ethnicity, respondent (self/proxy), smoking
			Exposure group			
			Unexposed	821	1.0	
			Ever exposed	33	0.9 (0.5–1.5)	
			Non-substantial exposure	25	0.9 (0.5–1.5)	
			Substantial exposure[a]	8	1.0 (0.3–2.7)	
			Level of exposure			
			Low	25	0.9 (0.5–1.7)	
			Medium	6	1.0 (0.3–3.3)	
			High	2	0.3 (0.07–1.9)	
			Duration of exposure			
			1–21 years	17	1.0 (0.5–2.0)	
			≥22 years	16	0.8 (0.4–1.6)	

CI, confidence interval

[a] Substantial exposure: medium or high level frequency ≥5% for at least 5 years, occurring at least 5 years before the interview.

associations were found with exposure to titanium dioxide and histological type of lung cancer. [The main limitations of this study are the reliance on self-reported occupational histories and expert opinion rather than measurement of exposure. A strength of this study was the availability of lifetime smoking histories and other covariates.]

2.4 References

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3. Studies of Cancer in Experimental Animals

The Working Group identified an issue that relates to the interpretation of several of the inhalation and intratracheal instillation studies of titanium dioxide. A lesion that is frequently seen in rats that have been exposed by inhalation to a range of poorly soluble particles such as titanium dioxide has been described variously as 'proliferating squamous cyst', 'proliferative keratinizing cyst', 'proliferating squamous epithelioma', 'benign cystic keratinizing squamous-cell tumour' or 'cystic keratinizing squamous-cell tumour'. Various authors have included this lesion in tumour counts, but the neoplastic nature of this lesion has been debated (Kittel *et al.*, 1993; Carlton, 1994; Mauderly *et al.*, 1994; Boorman & Seely, 1995; Rittinghausen *et al.*, 1997; Rittinghausen & Kaspareit, 1998); its relationship to pulmonary neoplasia is uncertain.

3.1 Oral administration

3.1.1 *Mouse*

Groups of 50 male and 50 female B6C3F$_1$ mice, 5 weeks of age, were fed diets containing 0, 2.5 or 5% titanium dioxide (size unspecified; anatase; purity, ≥98%) daily for 103 weeks. Mice were killed at 109 weeks of age, at which time no significant difference in survival was observed between treated and control males (32, 40 and 40 surviving animals in the control, low-dose and high-dose groups, respectively). In females, a dose-related trend in decreased survival was noted (*P*=0.001, Tarone test; 45, 39 and 33 survivors, respectively). No significant differences in body weights or incidence of tumours were observed between treated and control groups (National Cancer Institute, 1979).

3.1.2 *Rat*

Groups of 50 male and 50 female Fischer rats, 9 weeks of age, were fed diets containing 0, 2.5 or 5% titanium dioxide (size unspecified; anatase; purity, ≥98%) daily for 103 weeks. The rats were killed at 113 weeks of age, at which time no significant difference in survival was observed between treated and control groups of either sex (31, 37 and 36 surviving males and 36, 36 and 34 surviving females in the control, low-dose and high-dose groups, respectively). No significant differences in body weights or incidence of tumours were observed between treated and control groups (National Cancer Institute, 1979).

Groups of 50 male and 50 female Fischer 344 rats, 6 weeks of age, were fed diets containing 0, 1.0, 2.0 or 5.0% titanium dioxide-coated mica (flat platelets; longest dimension, 10–35 µm; 28% titanium dioxide; 72% mica) for up to 130 weeks. There was no evidence of a carcinogenic effect (Bernard *et al.*, 1990).

3.2 Inhalation exposure

3.2.1 *Mouse*

A group of 80 female Crl:NMRI BR mice, 7 weeks of age, was exposed by inhalation to ultrafine titanium dioxide (P25, Degussa, Germany; MMAD, 0.80 µm) for 18 hour per day on 5 days per week for up to 13.5 months (7.2 mg/m^3 for the first 4 months, then 14.8 mg/m^3 for 4 months and 9.4 mg/m^3 for 5.5 months) and then maintained in clean air for a further 9.5 months. A control group of 80 animals was maintained in clean air. The mortality rate was 50% in the titanium dioxide-treated group after 17 months versus 20% in the control group. After 23 months, the percentages of mice with adenomas/adenocarcinomas were 11.3%/2.5% in the titanium dioxide-treated group and 25%/15.4% in the controls. The lung tumour rate in the mice was not significantly influenced by exposure to titanium dioxide (according to the method of Hoel & Walburg) (Heinrich *et al.*, 1995).

3.2.2 *Rat*

Groups of 50 male and 50 female Sprague-Dawley rats, 8 weeks of age, were exposed by inhalation to 0 or 15.95 mg/m^3 titanium dioxide (99.9% <0.5 µm; purity unspecified) for 6 hour per day on 5 days per week for 12 weeks. The rats were killed at 140 weeks. Average survival was 116 and 113 weeks for control and treated males, and 114 and 120 weeks for control and treated females, respectively. At the end of the study, 39 and 44 control and treated males and 45 and 45 control and treated females, respectively, were still alive. No significant differences in body weights or incidence of tumours were observed (lung and other respiratory tract tumours were benign; other neoplasms seen in the lung were metastases from tumours of other sites) between treated and control groups (Thyssen *et al.*, 1978). [The Working Group noted the short duration of exposure.]

Groups of 100 male and 100 female CD rats, 5 weeks of age, were exposed by inhalation to 0, 10, 50 or 250 mg/m^3 titanium dioxide (rutile; 99% pure; MMAD, 1.5–1.7 µm; ~84% of dust particles <13 µm) for 6 hour per day on 5 days per week for 2 years, at which time all surviving rats were killed. No differences in mortality, body weights or clinical signs were observed. The incidence of lung tumours was increased in both male and female high-dose rats (adenomas: 2/79, 1/71, 1/75 and 12/77 ($P<0.001$) control, low-, mid- and high-dose males, respectively; 0/77, 0/75, 0/74 and 13/74 ($P<0.001$) females, respectively; squamous-cell carcinomas: 0/79, 0/71, 0/75 and 1/77 males and 0/77, 1/75, 0/74 and 13/74 ($P<0.001$) females, respectively). One anaplastic carcinoma occurred in a low-dose male (Lee *et al.*, 1985a,b, 1986). Difficulty was experienced in distinguishing between keratinizing squamous metaplasia and squamous-cell carcinomas (Trochimowicz *et al.*, 1988). The 15 squamous-cell carcinomas reported (Lee *et al.*, 1985a,b; 1986; Trochimowicz *et al.*, 1988) were re-evaluated by Warheit and Frame (2006), who described 11 of the squamous-cell carcinomas as non-neoplastic pulmonary keratinizing cysts.

Groups of 50 male and 50 female SPF Fischer 344 rats, 8 weeks of age, were exposed to titanium dioxide (5.0±0.7 mg/m^3; 99.5% rutile; MMAD, 1.1 µm) for 6 hour per day on 5 days per week or air only (control) for 24 months then maintained in clean air for a further 1.5 months. No treatment-related effects on lifespan or causes of death were observed. No differences in tumour development were seen between the groups (one adenoma and one adenocarcinoma in treated animals and two adenomas and one adenocarcinoma in controls) (Muhle *et al.*, 1989, 1995). [The Working Group noted the relatively low exposure concentration.]

A group of 100 female Wistar rats, 7 weeks of age, was exposed by inhalation to titanium dioxide (P25, Degussa, Germany; MMAD, 0.80 µm) for 18 hour per day on 5 days per week for up to 24 months (7.2 mg/m^3 for the first 4 months, then 14.8 mg/m^3 for 4 months and 9.4 mg/m^3 for 16 months) and then maintained in clean air for a further 6 months. A control group of 220 animals was maintained in clean air. After 30 months, 32/100 treated rats had lung tumours (20 benign squamous-cell tumours, three squamous-cell carcinomas, four adenomas and 13 adenocarcinomas) in contrast to only 1/217 controls (one adenocarcinoma). Lung tumour incidence was 19/100 when benign squamous-cell tumours were not included (Heinrich *et al.*, 1995).

3.3 Intratracheal administration

3.3.1 *Mouse*

Groups of 24 and 22 female A/J mice, 20 weeks of age, received a single intratracheal instillation of a suspension of 0.5 mg titanium dioxide (>99.9% pure; size unspecified) in saline or saline alone (control), respectively, and were maintained until 105 weeks of age. No differences in the incidence of lung tumours (17/24 versus 19/22 controls) or tumour multiplicity (2.24±1.35 versus 1.42±0.77) were noted (Koizumi *et al.*, 1993). [The Working Group noted the single administration of a low dose.]

3.3.2 *Rat*

Groups of 24 or 48 female SPF Wistar (HsdCpb:WU) rats, 8–9 weeks of age, received weekly intratracheal instillations under carbon dioxide anaesthesia of one of three types of titanium dioxide. The first type was P25: hydrophilic, majority anatase; mean particle size, ~0.025 µm; density, 3.8 g/mL; specific surface area, 52 m^2/g. The second type was P805 (AL 90 003-2): hydrophobic; mean particle size, 0.021 µm [data on T805 were available to the authors and the Working Group assumed that T805 was very similar to P805]; density, 3.8 g/mL; specific surface area, 32.5 m^2/g. The third type was AL 23 203-3: hydrophilic, anatase; mean particle size, ~0.2 µm; density, 3.9 g/mL; specific surface area, 9.9 m^2/g. The dusts were suspended by ultrasonification in 0.4 mL 0.9% phosphate buffered sodium chloride solution, and Tween 80® was added (1.0%) as a detergent to improve the homogeneity of the dosed suspensions. A control group was maintained untreated. Table 3.1 summarizes the experimental groups and the doses instilled. Rats were inspected for clinical signs of morbidity and mortality twice per weekday and once a day on weekends. The experiment was terminated at 30 months unless rats were killed when moribund or diagnosed with a growing subcutaneous tumour. Because of acute toxicity, the number of animals exposed to the hydrophobic titanium dioxide was reduced. After death of the animals and before necropsy of the thoracic and abdominal cavity, lungs were insufflated *in situ* with formalin via the trachea. In particular, the surface of the lung was inspected and lesions were recorded. Lungs were embedded in paraffin and sections were stained with haematoxylin-eosin. All suspected tumour tissues that were taken from other sites were also examined for histopathological lesions, especially for tumours that might be primary tumours with lung metastases. Table 3.1 also summarizes the lung tumour incidence of each group. Statistically significant increases in benign and/or malignant lung tumours were observed with both types of hydrophilic titanium dioxide (Pott & Roller, 2005).

Table 3.1. Dose schedules and incidence of tumours in female SPF Wister rats after intratracheal instillation of titanium dioxide

Type of titanium dioxide	Dose instilled	No. of rats at start/at risk[a]	50% survival (weeks)[b]	Lungs with benign tumours[c] (%)	Lungs with malignant tumours[c] (%)	Lungs with total tumours[c] (%)	Lungs with metastases of other tumours (%)
P25, hydrophilic	5×3 mg	48/42	114	21.4	31.0	52.4	14.3
	5×6 mg	48/46	114	17.4	50.0	67.4	15.2
	10×6 mg	48/46	104	23.9	45.7	69.6	15.2
P805, AL90,	15×0.5 mg[d]	24/11	86	0.0	0.0	0.0	9.1
hydrophobic	30×0.5 mg[d]	48/15	114	6.7	0.0	6.7	6.7
AL23, anatase,	10×6 mg	48/44	108	15.9	13.6	29.5	11.4
hydrophilic	20×6 mg	48/44	113	38.6	25.0	63.6	2.3
No treatment	–	48/46	113	0.0	0.0	0.0	13.0

From Pott & Roller (2005)

[a] Number of rats examined that survived at least 26 weeks after the first instillation.

[b] Period after first instillation in which 50% of the animals died excluding rats that died immediately after anaesthesia.

[c] Primary lung tumour types diagnosed; benign: adenoma, epithelioma; malignant: adenocarcinoma, squamous-cell carcinoma; lungs with one or more malignant tumours may additionally have had benign tumours.

[d] The doses had to be reduced because of unexpected acute toxicity.

3.3.3 *Hamster*

Groups of 24 male and 24 female Syrian golden hamsters, 6–7 weeks of age, received intratracheal instillations of 0 (control) or 3 mg titanium dioxide ([purity unspecified]; particle size: 97% <5 µm; 51% <0.5 µm) in 0.2 mL saline once a week for 15 weeks. The animals were observed until spontaneous death. All control and treated hamsters died by weeks 110–120 and 70–80, respectively, after the beginning of the experiment. The respiratory tract and other organs with gross lesions were examined histopathologically. No respiratory tract tumours were found in the treated groups compared with two tracheal papillomas that were found in untreated controls (Stenbäck *et al.*, 1976).

3.4 Subcutaneous injection

Rat

Groups of 20 male and 20 female Sprague-Dawley rats, 13 weeks of age, received a single subcutaneous injection into the flank of 1 mL saline (control) or 30 mg of one of three preparations of titanium dioxide (>99% pure, coated with antimony trioxide; >95% pure, coated with aluminium oxide; or >85% pure, coated with both compounds) in 1 mL saline. All rats were observed until spontaneous death, which occurred as late as 136, 126, 146 and 133 weeks in the control and three titanium dioxide-treated groups, respectively. No tumour was observed at the site of the injection in any group (Maltoni *et al.,* 1982). [The Working Group noted the inadequate reporting of the study.]

3.5 Intraperitoneal injection

3.5.1 *Mouse*

Groups of 30 or 32 male Marsh-Buffalo mice, 5–6 months of age, received a single intraperitoneal injection of 0 (control) or 25 mg titanium dioxide (purity, >98%; manually ground) in 0.25 mL saline, respectively. All survivors (10 control and 13 treated mice) were killed 18 months after treatment. No difference in the incidence of local or distant tumours was observed between treated and control animals (Bischoff & Bryson, 1982).

3.5.2 *Rat*

As part of a large study on various dusts, three groups of female Wistar rats [initial numbers unspecified] (9, 4 and 5 weeks of age, respectively) received intraperitoneal injections of titanium dioxide (P25, Degussa, Germany) in 2 mL 0.9% saline solution. The first group received a total dose of 90 mg/animal in five weekly injections; the second group received a single injection of 5 mg/animal; and the third group received three weekly injections of 2, 4 and 4 mg/animal. One concurrent group of Wistar rats (controls), 5 weeks of age, received a single injection of saline alone. Average lifespans were 120, 102, 130 and 120 weeks, respectively. No intra-abdominal tumour was reported in 47 and 32 rats that were examined in the second and third groups; six of 113 rats (5.3%) examined in the first group had sarcomas, mesotheliomas or carcinomas of the abdominal cavity [numbers unspecified]. Two of 32 controls (6.3%) had abdominal tumours [tumour type not specified]. In a similar experiment with female Sprague-Dawley rats that received single intraperitoneal injections of 5 mg/animal titanium dioxide, 2/52 rats (3.8%) developed abdominal tumours [tumour type not specified] (average lifespan, 99 weeks). [Controls were not available for comparison in this last experiment] (Pott *et al.*, 1987). [The Working Group noted the limited reporting of the study.]

Groups of female Fischer 344/Jslc rats [*n*=330; number of rats per group unspecified], 5 weeks of age, received intraperitoneal injections of one of several man-made mineral fibres, including titanium oxide (rutile) whiskers [fibre length, ~2.5 µm; fibre diameter, ~0.125 µm (estimated from a figure)]. The fibres were given in doses of 5, 10 or 20 mg with 1 mg of dust suspended in 1 mL saline before injection. The greatest volume administered in a week was 5 mL. The fibre concentration of titanium oxide whiskers was 639×10^3/µg. Two years after administration, peritoneal mesotheliomas were induced by silicon carbide whiskers (fibre concentration, 414×10^3/µg; cumulative incidence, 70–100%) and potassium titanate whiskers (fibre concentration, 594×10^3/µg; cumulative incidence, 20–77%) but not by titanium dioxide whiskers (Adachi *et al.*, 2001). [The Working Group noted the inadequate reporting of the study.]

3.6 Administration with known carcinogens

Hamster

Groups of 24 male and 24 female Syrian golden hamsters, 6–7 weeks of age, received intratracheal instillations of 3 mg titanium dioxide ([purity unspecified]; particle size: 97% <5 µm; 51% <0.5 µm) plus 3 mg benzo[*a*]pyrene in 0.2 mL saline or 3 mg benzo[*a*]pyrene alone in saline (controls) once a week for 15 weeks. Animals were observed until spontaneous death; all control and treated hamsters had died by 90–100 and 60–70 weeks, respectively. In the 48 hamsters treated with titanium dioxide plus benzo[*a*]pyrene, tumours [number of tumours per sex unspecified] occurred in the larynx (11 papillomas, five squamous-cell carcinomas), trachea (three papillomas, 14 squamous-cell carcinomas, one adenocarcinoma) and lung (one adenoma, one adenocarcinoma, 15 squamous-cell carcinomas, one anaplastic carcinoma). Two papillomas occurred in the trachea of benzo[*a*]pyrene-treated controls. In the same study, ferric oxide (3 mg) and benzo[*a*]pyrene induced a similar spectrum of tumours to that induced by the combination with titanium dioxide (Stenbäck *et al.*, 1976).

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4. Mechanistic and Other Relevant Data

The general principles of inhalation, deposition, clearance and retention of poorly soluble particles that have low toxicity are discusssed in the Monograph on carbon black in this volume.

4.1 Humans

4.1.1 *Deposition, retention and clearance*

Humans can be exposed to titanium dioxide via inhalation, ingestion or dermal contact. This section describes several case reports of pulmonary findings in humans exposed to titanium dioxide, a clinical study of absorption of titanium dioxide in the gastrointestinal tract and several studies that examined dermal effects and absorption of titanium dioxide from sunscreens.

The human pulmonary studies of titanium dioxide are largely limited to case reports of one or more highly exposed individuals that detail the location of large amounts of titanium dioxide in the tissues. Interpretation of these studies is complicated by co-exposures to other compounds (e.g. cigarette smoke and silica) and a lack of information regarding the estimated delivered pulmonary doses. Therefore, clearance kinetics following acute and chronic exposure to titanium dioxide are poorly characterized in humans relative to animals.

The autopsy of a 55-year-old man was conducted approximately four years after four years of 'heavy' exposure to titanium dioxide (rutile) (Rode *et al.*, 1981). The surface of the lungs showed numerous white deposits (1–2 mm in diameter) beneath the intact pleura. Within the lungs, the same white pigment was found fairly evenly distributed among all lobes. The pigment was mainly distributed around the perivascular tissue, but small amounts were found in alveolar walls and in alveolar macrophages. Lymph nodes also contained large amounts of pigment.

Gylseth *et al.* (1984) reported the case of a 53-year-old nonsmoking male farmer who had a mixed dust pneumoconiosis and a lung tumour. The lobe that contained the tumour was removed and analysed. Mineral dusts were deposited in peribronchial and perivascular areas, within alveolar macrophages in the peripheral lung or as small granular accumulations in the interstitium. Dusty deposits were accompanied by local fibrosis. Of the fibres identified, 63% were rutile fibres (0.76–5.5 μm) and 37% were amphibole asbestos (0.7–9 μm).

Yamadori *et al.* (1986) reported the case of a 53-year-old man with pneumoconiosis due to approximately 13 years of occupational exposure to 'high' concentrations of titanium dioxide. The patient died of lung cancer, which was possibly associated with a 34 pack–year smoking history and not attributed to exposure to titanium dioxide. At autopsy, about 9–10 years after the exposures to titanium dioxide, particle deposition was found to be diffuse in the lung and particles were typically found in interstitial and alveolar macrophages. Examination of lung tissue in the right upper lobe and right hilar lymph nodes showed deposits of crystalloid substances that had a high titanium content and measured 0.2–0.3 μm by 0.7 μm.

Moran *et al.* (1991) analysed lung sections from three male patients (46–57 years of age) with potential occupational exposure to titanium dioxide. Large quantities of dark granular pigment were found in macrophages in the alveolar spaces and around the bronchioles and blood vessels. X-Ray crystallography showed that the lungs of all the patients contained rutile and silica and that those of two of the patients also contained talc.

Böckmann *et al.* (2000) determined blood levels of titanium dioxide (anatase) following oral ingestion of titanium-dioxide capsules and/or powder in six adult men (24–66 years of age). Titanium dioxide was absorbed by the gastrointestinal tract in a size-dependent manner: smaller particles (0.16 μm) were more readily absorbed than larger ones (0.38 μm). Before the experiment, the background blood levels of titanium dioxide in these men ranged from ~6 to 18 μg/L. Blood levels reached up to ~50 μg/L or 100 μg/L between 4 and 12 hours after intake of 23 mg or 46 mg titanium dioxide, respectively.

In a study of 13 Caucasian skin-surgery patients (four women and nine men aged 59–82 years) who applied a microfine (10–50 nm) titanium-dioxide sunscreen for 9–31 days, Tan *et al.* (1996) found that tissue levels overlapped with those in skin samples collected post-mortem. Furthermore, there was no correlation between duration of sunscreen application and the measured concentrations of titanium dioxide. After 4 days of sunscreen application, Lademann *et al.* (1999) also reported that the deeper layers of the stratum corneum were devoid of titanium dioxide. Pflücker *et al.* (2001) performed tests with three sunscreens that contained different types of titanium dioxide (20 nm, cubic; 100 nm, needles; and 100 nm, needles composed of aggregated 10–15-nm particles). At six hours after application, punch biopsies were taken from each area. Consistent with the in-vitro study by Gamer *et al.* (2006), titanium dioxide pigments were located exclusively on the outermost layer of the stratum corneum in all cases. [The Working Group noted the lack of studies on penetration of titanium dioxide in compromised skin, and that a flex skin model was never used to address this issue.]

4.1.2 *Toxic effects*

None of the case reports provided quantitative industrial hygiene information about the exposure of workers to titanium-dioxide dust.

A small set of studies from the titanium industry where ilmenite (iron titanate) was the dust probably involved in exposure has been reviewed (IARC, 1989).

Many case studies have reported abnormalities related to exposure to titanium. In some, titanium dioxide was still identified in the lungs of workers exposed to respirable titanium dioxide years after exposure had ceased. Some case studies reported varying degrees of fibrogenic changes to the lung associated with either brief or extended high-level exposures (Elo *et al.*, 1972; Määttä & Arstila, 1975). In contrast, others that involved exposure to titanium dioxide pigment materials showed no evidence of lung inflammation or fibrosis (Schmitz-Moormann *et al.*, 1964; Rode *et al.*, 1981).

Elo *et al.* (1972) reported pulmonary fibrosis or fibrotic changes and alveolar macrophage responses that were identified by thoracotomy or autopsy tissue sampling in three workers who had been employed for 6–9 years in dusty work in a titanium-dioxide factory. No data on workplace exposure were reported. Two workers were 'moderate' or 'heavy' smokers but smoking information was not provided for the third worker. Small amounts of silica were present in all three lung samples and significant amounts of nickel were present in the lung tissue of the autopsied case. Exposure was confirmed using sputum samples that contained macrophages with high concentrations of titanium 2–3 years after their last exposure (Määttä & Arstila, 1975). Titanium particles were identified in the lymph nodes of the autopsied case. The lung concentrations of titanium were higher than those of control autopsy specimens from patients who had not been exposed to titanium dioxide.

A case of granulomatous lung disease was reported in a worker who had possibly been exposed to titanium dioxide at an aluminium smelting plant where he had worked near a firebrick furnace. A lymphocyte transformation test showed a proliferative response to titanium chloride but not to any other metal tested, which suggested a possible link with titanium hypersensitivity (Redline *et al.*, 1986).

Yamadori *et al.* (1986) reported titanium dioxide-associated pneumoconiosis in a male titanium-dioxide packer with 13 years of potential dust exposure and a 40-year history of smoking.

In a cross-sectional study of 209 titanium metal production workers, 78 of whom were involved in the reduction process and were exposed to titanium-tetrachloride vapour, titanium oxychloride and titanium-dioxide particles had reductions in lung function (Garabrant *et al.*, 1987). The authors noted that this finding could be due to exposure to titanium tetrachloride, which reacts violently with water to liberate heat and produce hydrochloric acid, titanium oxychloride and titanium dioxide. Pleural disease with plaques and pleural thickening was observed in 36 of the 209 workers, including eight of the 78 reduction-process workers. Some cases were probably caused by previous exposure to asbestos; however, among workers who were not known to have been exposed to asbestos, the risk for pleural disease after more than 10 years of employment was 3.8 times that in workers who had been employed for less than 5 years.

Oleru (1987) studied 67 workers in a small titanium oxide paint factory in Nigeria. Airway symptoms were reported by 50–54%, neurological symptoms by 20–40% and other symptoms by 10–27% of the workers. The symptoms were correlated to exposure and with pulmonary function tests. Twenty-eight cases of restrictive lung impairment were observed. Smoking prevalence was low, but several of the workers were also exposed to cotton dust.

A chest X-ray study of 336 workers at two titanium dioxide-production plants showed 19 cases of pleural abnormalities (thickening or plaques) compared with three cases among 62 unexposed workers at the same plants (Chen & Fayerweather, 1988). The odds ratio for chest X-ray abnormality associated with exposure to titanium dioxide was 1.4, although exposures at the plants included titanium tetrachloride, potassium titanate and asbestos. No lung fibrosis was observed.

Moran *et al.* (1991) reported exposure to titanium dioxide in four men and two women. Diffuse fibrosing interstitial pneumonia and bronchopneumonia were reported in three male patients (a titanium dioxide worker, a painter and a paper mill worker) with deposits of titanium dioxide (rutile) in the lung and smaller amounts of silica deposited in the tissues. Smoking information was not reported.

Keller *et al.* (1995) reported a case of pulmonary alveolar proteinosis (i.e. deposition of proteinaceous and lipid material within the airspaces of the lung) in a worker who had been employed for more than 25 years as a painter, with eight years of experience in spray painting, and who smoked two packs of cigarettes per day until he was hospitalized. Titanium was the major type of metallic particle found in his lung tissues.

4.2 Experimental systems

4.2.1 *Deposition, retention and clearance*

A considerable number of toxicological studies, both *in vivo* and *in vitro*, have characterized the disposition (deposition, absorption, distribution and elimination) of titanium dioxide particles in the respiratory tract of animals and cells. Experimental protocols and findings of many of these studies are provided in Tables 4.1–4.3.

Most animal studies on the effects of titanium dioxide on the respiratory tract have been conducted in rats. Generalizations with regard to the effects of inhaled particle size on the amount and site of deposition in the lungs and subsequent clearance are applicable to animals as well as humans and can be made but with some caution. A variety of factors other than particle parameters can influence delivered dose, distribution within the lungs and subsequent clearance. These factors complicate comparisons between studies and interspecies extrapolation of observed effects. Hence, some caution must be advised when comparing results among the various studies in Tables 4.1–4.3. For example, Bermudez *et al.* (2002) exposed rats, mice and hamsters to the same particle size, at the same particle concentration, for the same exposure time. However, despite the same study design, similar doses would not necessarily be received between the species. At a concentration of 250 mg/m^3, mice had a larger normalized pulmonary particle burden than rats and hamsters (170, 120 and 114 mg/g dry lung, respectively).

Normalized particle dose (deposited mass per body weight) delivered to the respiratory tract may decrease with increasing animal size. This was the observation of McMahon *et al.* (1975), who compared aerosol (gold particles, 0.78 µm MMAD) deposition in mice, hamsters, rats, rabbits and dogs. Ferin and Morehouse (1980) also

Table 4.1. Inhalation studies of titanium dioxide (TiO_2) disposition and responses in animal models

Species, sex (age/weight)	Aerosol characteristics	Exposure concentration	Exposure protocol	Observed effect(s)	Reference
Hooded rats of Long-Evans descent (~250 g)	TiO_2,1.48 µm MMAD (σ_g=3.26); NO_x or SO_2 + TiO_2	100 mg/m^3 for 2, 4 or 6 h; after gaseous exposure, aerosol at 15 mg/m^3 for 7 h	About 10 rats in each group killed at 1, 8, 25 and 130 days after exposure	In non-pollutant-exposed rats, about 40% of TiO_2 cleared by 25 days and 80% cleared by 130 days after inhalation; based on a linear association between TiO_2 levels in the trachea and lung burden, authors suggested that particles were removed from the alveoli via the airways by alveolar macrophages. NO_x and SO_2 stimulated clearance at low-exposure levels and suppressed clearance at higher exposure levels.	Ferin & Leach (1975)
Long-Evans and Fischer 344 rats, male (9 weeks)	TiO_2, 1.0 µm MMAD (σ_g=2.3)	14.9 mg/m^3 for 7 h	10 rats killed at 1, 8, 25 and 130 days after exposure	At days 1 and 25 after exposure, TiO_2 content in lung lobes was significantly associated with lobe weight in both rat strains. The distribution of TiO_2 between lobes was similar between strains. Normalized to lung weight, the smaller Fischer 344 rats received a slightly greater total lung burden than the Long-Evans rats (114 versus 105 µg/g lung). Lung clearance between days 1 and 8 was greater in the Long-Evans than in the Fischer 344 rats, although subsequent clearance rates were quite similar between the strains. At 25 days, 55 and 70% retention was observed in Long-Evans and Fischer 344 rats, respectively. Authors suggested that there may be strain differences affecting early alveolar clearance mechanisms.	Ferin & Morehouse (1980)

Table 4.1 (contd)

Species, sex (age/weight)	Aerosol characteristics	Exposure concentration	Exposure protocol	Observed effect(s)	Reference
Long-Evans rats, male (~300 g)	TiO_2 (anatase), 1.0 µm MMAD (σ_g=2.3), aerosol-as-generated and charge-neutralized aerosols	10.8–15.5 mg/m^3	Rats exposed for 7 h; deposition assessed in 40 rats; clearance assessed at 1, 8, and 25 days after exposure (20 rats per time-point)	On average, the deposition efficiency was 79% for charge-neutralized aerosols and 100% for aerosols-as-generated by a Wright dust feeder. The pattern of deposition within the lungs was unaffected by particle charge as indicated by a no-charge-effect on clearance.	Ferin *et al.* (1983)
Long-Evans rats, males (~300 g)	TiO_2 (anatase), 1.0 µm MMAD (σ_g=2.3); TiO_2 (rutile), 0.83 µm MMAD (σ_g=2.02)	16.5±1.7 mg/m^3, 19.3±3.1 mg/m^3	Rats exposed for 7 h; 8–10 rats killed at 1, 8, 27 and 132 days after exposure	Crystal structure had no effect on pulmonary particle clearance (half-times of 51 and 53 days for anatase and rutile, respectively).	Ferin & Oberdörster (1985)
Crl:CD rats	TiO_2 (rutile), 1.5–1.7 µm MMAD	10, 50, 250 mg/m^3	Four exposure groups of 100 male and 100 female rats exposed 6 h/day, 5 days/week up to 2 years; rats killed at 3, 6, 12 and 24 months.	No abnormal clinical signs, body weight changes or excess mortality in any group compared with controls; at 10 mg/m^3, particles were mostly phagocytosed by alveolar macrophages. At 50 mg/m^3, there was marked hyperplasia of alveolar lining cells with some alveoli adjacent to terminal bronchioles exhibiting ciliated cells; macrophages containing dust were aggregated; cellular debris, proteinosis and fibrosis were observed. Lung weights at 250 mg/m^3 were double those of the 10-mg/m^3 and control groups. Dose-related increase in particle number identified in tracheobronchial lymph nodes, cervical lymph nodes, liver and spleen was observed. Animal grooming could have been the source of the observed extrapulmonary particles.	Lee *et al.* (1985a,b, 1986)

Table 4.1 (contd)

Species, sex (age/weight)	Aerosol characteristics	Exposure concentration	Exposure protocol	Observed effect(s)	Reference
Wistar rats, female	TiO_2 (anatase), 4.8 μm MMAD, 15–40-nm primary particles	8.6 mg/m^3	6 rats exposed to each aerosol for 7 h/day for 1 year	TiO_2 particles observed mainly in interstitial macrophages of the alveolar walls; these were frequently aggregated in small granulomas. Lesions associated with TiO_2 particle accumulation distributed throughout alveolar region	Takenaka *et al.* (1986)
PVG rats, male (12 weeks)	TiO_2 (rutile); quartz	10 mg/m^3	Exposed 7 h/day, 5 days/week up to 15 weeks; 4 rats per group killed at days 2, 4, 8, 16, 32, 52, and 75; also, groups of 4 killed 62 days after exposure for 32 and 75 days	Macrophages were predominant cell type in lavages of unexposed controls. Macrophage and PMN levels in TiO_2 group remained at control levels for entire exposure period. Total lavage protein relative to TiO_2 was only slightly increased relative to controls.	Donaldson *et al.* (1988)
Long-Evans rats, male (220–260 g)	TiO_2, 1 μm MMAD (σ_g=1.4) after $CdCl_2$, 0.4–0.5 μm MMAD (σ_g=1.4–1.6) or before $CdCl_2$, 0.5 μm MMAD (σ_g=1.4)	13.3 mg/m^3 (TiO_2); 1.5, 5, 5 mg/m^3 ($CdCl_2$)	Rats (180 total) exposed nose-only to $CdCl_2$ followed 12 h after by TiO_2 for 6 h or vice versa to assess effect of Cd on particle clearance kinetics; burden of TiO_2 exposure assessed on days 1, 8, 15, 25 and 46	Relative to saline controls, the overall pulmonary clearance of TiO_2 not affected by $CdCl_2$ inhalation; however, 5-mg/m^3 exposures to $CdCl_2$ (either before or after TiO_2 inhalation) caused in increase in the amount of TiO_2 found in the lymph nodes relative to control and 1.5 mg/m^3 $CdCl_2$ which did not differ. Authors hypothesized that the cytotoxicity of $CdCl_2$ caused a decrease in macrophage clearance and an increase in transport to lymph nodes although changes in epithelial permeability could not be entirely ruled out.	Greenspan *et al.* (1988)

Table 4.1 (contd)

Species, sex (age/weight)	Aerosol characteristics	Exposure concentration	Exposure protocol	Observed effect(s)	Reference
Rats	TiO_2 (rutile),1.1 µm MMAD (σ_g=1.6), 200–700-nm primary particles; TiO_2 (anatase), 1.0 µm MMAD (σ_g=1.9), 20–40-nm primary particles; carbon black, 1 µm MMAD (σ_g=2), 14-nm primary particles	5 mg/m^3; 1, 4, 16 mg/m^3; 9.8 mg/m^3; 9 mg/m^3	30 h/week for 3 months; 30 h/week for 22.5 months; 95 h/week for 7 months; 95 h/week for 4.5 months	In general, clearance kinetics of polystyrene (3.5-µm spheres, ^{85}Sr-labelled) appeared to decrease with increasing volume burden of test materials. Despite having a lower volume burden and larger primary particle size, however, the ultrafine TiO_2 (anatase) tended to clear more slowly than carbon black (half-time 788 versus 420 days, respectively). Fine TiO_2 (rutile) caused a modest reduction in clearance relative to control (half-time 94 versus 74 days, respectively).	Muhle *et al.* (1990)
Fischer 344 rats, male and female (4 weeks)	TiO_2 (rutile), 1.0 µm MMAD (σ_g=1.6), 200–700-nm primary particles	5 mg/m^3	Rats (~12 per time-point and outcome) exposed 6 h/day, 5 days/week for up to 24 months; clearance measured from 15–100 days *in vivo* following acute inhalation of tracer aerosols: 3.5 µm ^{85}Sr-polystyrene and 0.26–0.39 µm $^{59}FeO_2$	Pulmonary clearance rates decreased in unexposed controls during study. Clearance rates in TiO_2-exposed rats were comparable with controls. Lung burden per mass of lung tissue was similar between males and females. At 15 months of TiO_2 exposure, rats had a small but significant decrease in macrophage levels and an increase in PMNs relative to controls. Epithelial permeability was not affected by TiO_2.	Muhle *et al.* (1990) [clearance kinetics, particle sizes]; Bellmann *et al.* (1991) [clearance kinetics]; Muhle *et al.* (1991) [particle sizes, cytology]

Table 4.1 (contd)

Species, sex (age/weight)	Aerosol characteristics	Exposure concentration	Exposure protocol	Observed effect(s)	Reference
Fischer 344 rats, male (180–200 g)	TiO_2 (anatase), 1.0 µm MMAD (σ_g=2.6)	50 mg/m^3	Rats exposed 6 h/day for 5 days and killed 1, 2, 4 and 9 weeks after exposure	One day after exposure, lung burden was 1.8 mg/lung for TiO_2. At 28 days after exposure, retention was 39%. Inhalation caused lesser effects, e.g. permeability and PMN influx, than instillation of similar lung burdens reported earlier (Driscoll *et al.*, 1990).	Driscoll *et al.* (1991)
Fischer 344 rats (240–260 g)	TiO_2 (anatase), 0.78 µm MMAD (σ_g=1.7), 21-nm primary particles; TiO_2 (anatase), 0.71 µm MMAD (σ_g=1.9), 250-nm primary particles	23.5±3.2 mg/m^3; 23.0±4.1 mg/m^3	Chamber exposure for 6 h/day, 5 days/week, for up to 12 weeks; rats killed at 4, 8, 12, 41 and 64 weeks; 4 rats per group, except only three in 41-week group	Retention half-times were 501 and 174 days for ultrafine (21 nm) and fine (250 nm) primary particles, respectively. As a percentage of total lung burden, the unlavageable fraction of particles plus particles in the hilar lymph node were also significantly greater for ultrafine than fine primary particles at 12, 41 and 64 weeks. On average, PMN influx due to ultrafines was 43-fold and 22-fold greater than that for fine particles at weeks 8 and 12 of exposure, respectively. By week 64, PMN levels had approached control levels for both aerosols.	Ferin *et al.* (1992)

Table 4.1 (contd)

Species, sex (age/weight)	Aerosol characteristics	Exposure concentration	Exposure protocol	Observed effect(s)	Reference
Fischer 344 rats	TiO_2 (anatase), 0.78 µm MMAD (σ_g=1.7), 21-nm primary particles; TiO_2 (anatase), 0.71 µm MMAD (σ_g=1.9), 250-nm primary particles	23.5±2.9 mg/m^3; 22.3±4.2 mg/m^3; 1.3±0.3 mg/m^3	Rats exposed to aerosols (6 h/day, 5 days/week, 12 weeks); subsequently, 4 rats inhaled and 4 rats instilled with tracer aerosol (3.3 µm, ^{85}Sr-labelled polystyrene); ^{85}Sr measured *in vivo* for 180 days	Ferin *et al.* (1992) reported pulmonary retention half-times of 501 and 174 days for inhaled aerosol composed of ultrafine (21 nm TiO_2) and fine (250 nm TiO_2) primary particles, respectively. After TiO_2 exposure, inhaled/instilled polystyrene had slow-phase clearance half-times of 66/72 days (control), 117/99 days (250 nm TiO_2), 541/606 days (21 nm TiO_2). Accelerated tracheobronchial clearance was observed when pulmonary clearance was retarded. For both TiO_2 aerosols, the exposure-induced PMN influx appeared related to particle surface area. Ultrafine TiO_2 induced focal interstitial pneumonia and focal alveolitis.	Oberdörster *et al.* (1994, 1997)
Fischer 344 rats (175–225 g)	TiO_2, (anatase) fine (250 nm) and ultrafine (21 nm) particles delivered as aggregates with 1.0–1.2 µm MMAD (σ_g=1.6–2.2)	125 mg/m^3	Rats exposed for 2 h via endotracheal tube while anaesthetized and ventilated; rats (6 per time-point) killed at 0, 1, 3 and 7 days after exposure; pattern of deposition evaluated in 3 rats	Pattern of deposition (TiO_2 mass deposited per lobe) was well correlated with lung lobe size (% total lung weight). Immediately after exposure, total lavage protein significantly increased 7-fold and 3-fold in ultrafine and fine TiO_2 exposure groups, respectively, relative to unexposed controls. One day after exposure, protein levels remained increased by 3-fold in ultrafine exposure group. Significant PMN influx occurred in ultrafine exposure group relative to unexposed controls 1 day after exposure. Comparison of responses as a function of primary particle size was confounded by ~40% greater ultrafine than fine particle mass dose 1 day after exposure.	Osier & Oberdörster (1997)

Table 4.1 (contd)

Species, sex (age/weight)	Aerosol characteristics	Exposure concentration	Exposure protocol	Observed effect(s)	Reference
Crl:CDBR rats, male (7–8 weeks)	TiO_2 (rutile),1.7 µm MMAD, 0.25 µm primary particles	5, 50, 250 mg/m^3	Rats exposed 6 h/day, 5 days/week for 4 weeks; killed at 0 h, 1 week, 1, 3 and 6 months after exposure	After exposure to 5, 50, and 250 mg/m^3, lung burdens for TiO_2 were approximately 0.26, 2.7, and 12 mg, respectively. Clearance rates decreased with increasing exposure concentrations; TiO_2 half-times were 68, 110, and 330 days for 5, 50, and 250 mg/m^3, respectively. Number of particles in lymph nodes was increased in the highest exposure group relative to other exposure and control groups. The highest exposure group also had focal hypertrophy and hyperplasia which were associated with aggregates of pigmented macrophages in alveoli and at alveolar duct bifurcations. These focal lesions were evident for the entire follow-up periods. At 3 months after exposure to 250 mg/m^3 TiO_2, chemotaxis of alveolar macrophages was also reduced. Fibrosis was not observed to any significant degree in any groups.	Warheit *et al.* (1997)

Table 4.1 (contd)

Species, sex (age/weight)	Aerosol characteristics	Exposure concentration	Exposure protocol	Observed effect(s)	Reference
Syrian golden hamsters, male and female (4 weeks)	TiO_2 (rutile), 1.1 µm MMAD (σ_g=1.6), 200–700-nm primary particles	40 mg/m^3 for 5 months, then 30 mg/m^3	Animals (~9 per time-point and outcome) exposed 6 h/day, 5 days/week for up to 18 months; clearance measured 15–100 days *in vivo* following acute inhalation of tracer aerosol (3.5 µm ^{85}Sr-polystyrene)	TiO_2-exposed females tended to have slower clearance rates than similarly exposed males. On average, retention half-times in TiO_2-exposed hamsters were significantly reduced relative to controls at 3 months (control, 78 days; TiO_2, 226 days) and more so at 9 months (control, 115 days; TiO_2, 1120 days). However, at 15 months of TiO_2 exposure, clearance was more similar to controls (control, 88 days; TiO_2, 123 days). Intragroup variability in clearance rates was double that reported for rats by Bellmann *et al.* (1991). Authors suggested possible adaptation capability in hamsters.	Creutzenberg *et al.* (1998)
Wistar rats, male (12 weeks)	TiO_2 (rutile), 2.1 µm MMAD (σ_g=2.2)	25, 50 mg/m^3	Rats exposed 7 h/day, 5 days/week for up to 7 months; typically, 6 rats lavaged and 6 used to assess lung burden at each of 6 time-points	At end of exposures, lung burdens were 17 and 24 mg/g dry lung for low and high exposures to TiO_2. Macrophage levels did not change statistically during exposures. Lymph node burdens and PMN levels rapidly increased with TiO_2 exposures. Findings best associated with lung burden in terms of retained particle surface area. Lymph node burdens and PMN levels increased rapidly beyond a 'threshold' lung burden of 200–300 cm^2 particle surface area.	Cullen *et al.* (2000); Tran *et al.* (2000)

Table 4.1 (contd)

Species, sex (age/weight)	Aerosol characteristics	Exposure concentration	Exposure protocol	Observed effect(s)	Reference
Fischer 344 rats, female (6 weeks); B3C3F$_1$ mice, female (6 weeks); hamsters, female (6 weeks)	TiO_2 (rutile), 1.36–1.44 µm MMAD (σ_g=1.50–1.71), 220-nm primary particles	10, 50, 250 mg/m^3	Total of 65 rats, 65 mice and 73 hamsters exposed 6 h/day, 5 days/week, for 13 weeks; animals killed at 0, 4, 13, 26 and 52 (46 for hamsters) weeks after exposure	TiO_2 pulmonary retention half-time for the low-, mid- and high-exposure groups, respectively: 100, 324 and 838 days in rats; 50, 417 and 621 days in mice; and <110 days in hamsters. In rats and mice, PMN levels were significantly elevated in mid- and high-exposure groups and gradually decreased after exposure. However, the rate of PMN decline was far more gradual in the high-exposure groups, especially in rats. PMN levels in the high-exposure group of hamsters responded similarly to mid-exposure groups of mice and rats. In high-exposure groups of rats and mice, epithelial permeability remained elevated (>5 times low-exposure groups) up to 52 weeks, with no signs of recovery.	Bermudez *et al.* (2002)
Fischer 344 rats, female (6 weeks); B3C3F1 mice, female (6 weeks); hamsters, female (6 weeks)	TiO_2, 1.29–144 µm MMAD (σ_g=2.46–3.65), 21-nm primary particles	0.5, 2, 10 mg/m^3	Groups of 25 animals per species and time-point; animals exposed 6 h/day, 5 days/week, for 13 weeks and animals killed at 0, 4, 13, 26 and 52 (49 for hamsters) weeks after exposure	TiO_2 pulmonary retention half-times for the low-, mid- and high-exposure groups, respectively: 63, 132 and 365 days in rats; 48, 40 and 319 days in mice; and 33, 37 and 39 days in hamsters. In high-exposure groups of mice, epithelial permeability remained elevated (~twice control groups) up to 52 weeks without signs of recovery. Epithelial permeability was 3–4 times the control in high-dose rats through to 4 weeks after exposure, but approached control by 13 weeks. Epithelial permeability was unaffected in all groups of hamsters.	Bermudez *et al.* (2004)

Table 4.1 (contd)

Species, sex (age/weight)	Aerosol characteristics	Exposure concentration	Exposure protocol	Observed effect(s)	Reference
Wistar rats, adult male (250±10 g)	TiO_2, 22 nm CMD (σ_g=1.7), spark generation	0.11 mg/m^3, 7.3×10^6/cm^3	10 rats exposed 1 h via endotracheal tube while anaesthetized and ventilated at constant rate; lungs fixed at 1 or 24 h after exposure	Distributions of particles among lung compartments followed the volume distribution of compartments and did not differ significantly between 1 and 24 h post-inhalation. On average, 79.3±7.6% of particles was on the lumenal side of the airway surfaces, 4.6±2.6% was in epithelial or endothelial cells, 4.8±4.5% was in connective tissues and 11.3±3.9% was within capillaries. Particles within cells were not membrane-bound.	Geiser *et al.* (2005)

$CdCl_2$, cadmium chloride; CMD, count median diameter; MMAD, mass median aerodynamic diameter; NO_x; nitrogen oxide; PMN, polymorphonuclear neutrophils; SO_2, sulfur dioxide

Table 4.2. Instillation studies of titanium dioxide (TiO_2) disposition in animal models

Species, sex (age/weight)	Characteristics of particles and exposure	Exposure protocol	Observed effect(s)	Reference
Long-Evans rats (~300 g)	TiO_2 (rutile), 0.5, 5 mg/rat; TiO_2 (anatase), 0.5, 5 mg/rat	6 male rats per group instilled with each material in 0.2 mL saline; two control groups: non-instilled and saline-instilled; lung lavaged at 24 h after instillation.	No indication that crystal structure affected biological outcomes. High TiO_2 doses (5 mg) caused significant PMN influx relative to control and lower TiO_2 doses. Small but significant increase in macrophages after 0.5 mg rutile instillation relative to high TiO_2 doses (both rutile and anatase).	Ferin & Oberdörster (1985)
BALB/c BYJ mice, male, (7–8 weeks, ~27 g)	TiO_2 1.57 µm MMAD (σ_g=2.3), 11.8 µg/mouse	Mice (3 per group and time-point) instilled with each material in 20 µL phosphate buffered saline and killed at 6 periods between 15 min and 7 days	PMN levels in TiO_2 groups did not differ relative to saline controls at 20 h, 3 days or 7 days after instillation. Lung clearance half-time was 19 days for TiO_2.	Finch *et al.* (1987)
Fischer 344 rats, male (180–200 g)	TiO_2 (anatase, 2.1±1.5 µm), 5, 10, 50, 100 mg/kg bw	5–6 rats per exposure group killed 1, 7, 14 and 28 days after-instillation; 5-mg/kg dose not assessed at day 1	At all but the lowest instilled dose, TiO_2 caused increased PMN levels relative to saline controls at all time-points. At 5-mg/kg TiO_2, PMN levels were only increased at day 7. At 28 days following 50 mg/kg, TiO_2 was found primarily in macrophages located at the alveolar duct levels.	Driscoll *et al.* (1990)

Table 4.2 (contd)

Species, sex (age/weight)	Characteristics of particles and exposure	Exposure protocol	Observed effect(s)	Reference
Fischer 344 rats, male (240–260 g)	12-nm TiO_2 (rutile), 500 µg/rat; 21-nm TiO_2 (anatase), 65, 107, 200, 500, 1000 µg/rat; 230-nm TiO_2 (rutile), 500 µg/rat; 250-nm TiO_2 (anatase), 500, 1000 µg/rat	3–8 rats per group killed 24 h after exposure	For doses >500 µg, the unlavageable fraction appeared to correlate with instilled number of particles and decreased with increasing particle diameter.	Ferin *et al.* (1992)
Fischer 344 rats, male (~220 g)	12-nm TiO_2 (rutile), 500 µg/rat; 20-nm TiO_2 (anatase), 65, 107, 200, 500, 1000 µg/rat; 220-nm TiO_2 (rutile), 500 µg/rat; 250-nm TiO_2 (anatase), 500, 1000 µg/rat; 20-nm TiO_2 (anatase, serum-coated), 100 µg/rat; 20-nm TiO_2 (anatase, phagocytosed), 104 µg/rat	4–10 rats per group killed 24 h after exposure	Fraction of particles retained in tissues (epithelial cells or interstitium) and protein leakage correlated with surface area of retained particles. Serum coating did not affect inflammatory response or protein leakage. Phagocytosed particles did not access the tissues or induce an inflammatory response.	Oberdörster *et al.* (1992a)

Table 4.2 (contd)

Species, sex (age/weight)	Characteristics of particles and exposure	Exposure protocol	Observed effect(s)	Reference
Fischer 344 rats, male (175–225 g)	Fine (250 nm) TiO_2 (anatase), 500 µg/rat; ultrafine (21 nm) TiO_2 (anatase), 750 µg/rat	Rats instilled with particles in 0.2 mL saline (6 per time-point) and killed 0, 1, 3 and 7 days after exposure	Significantly increased PMN influx in rats exposed to ultrafine particles via instillation relative to inhalation and unexposed controls at 1, 3 and 7 days after exposure. Rats instilled with fine particles had a significant increase in PMNs relative to unexposed rats 1 day after exposure only. Significantly increased number of macrophages was present 3 and 7 days after ultrafine instillation relative to inhalation and unexposed controls. Comparison of responses as a function of primary particle size was confounded by ~40% greater ultrafine than fine particle mass dose 1 day after exposure.	Osier & Oberdörster (1997)

Table 4.2 (contd)

Species, sex (age/weight)	Characteristics of particles and exposure	Exposure protocol	Observed effect(s)	Reference
Fischer 344 rats, males (10 weeks; TiO_2 only, 211±10 g; endotoxin plus TiO_2, 235±39 g); C57BL/6J mice, male (23.3±1.6 g, TiO_2 only)	Ultrafine (20 nm) TiO_2 (anatase), 31, 125, 500 µg/rat; 6, 25, 100 µg/mouse; fine (250 nm) TiO_2 (anatase), 125, 500, 2000 µg/rat; 25, 100, 400 µg/mouse; endotoxin before ultrafine TiO_2, 70 endotoxin units, 50 µg/rat; endotoxin before fine TiO_2, 70 endotoxin units, 50 µg/rat	TiO_2 exposure only: 3 animals per group killed at 6, 24 and 48 h after instillation; endotoxin plus TiO_2: instilled with TiO_2 30 min after endotoxin inhalation and killed 24 h after instillation	On the basis of instilled particle mass, ultrafine TiO_2 caused far greater PMN influx than fine particles in both rats and mice at all time-points. Expressed as instilled particle surface area, PMN responses to fine and ultrafine TiO_2 appeared to be similar. In endotoxin-primed rats, ultrafine TiO_2 caused a significant amplification of the PMN response relative to ultrafine TiO_2 or endotoxin alone, whereas fine TiO_2 did not elicit a significant response relative to controls.	Oberdörster *et al.* (2000)
Wistar rats, male (370–470 g)	29-nm TiO_2, 125, 500 µg/rat; 250-nm TiO_2, 125, 500 µg/rat	Rats killed 24 h after exposure	Epithelial permeability, epithelial damage and inflammation were increased following 500 µg instillation of ultrafine particles (29-nm TiO_2) but not fine particles (250-nm TiO_2)	Renwick *et al.* (2004)

bw, body weight; MMAD, mass median aerodynamic diameter; PMN, polymorphonuclear neutrophils

Table 4.3. In-vitro studies of titanium dioxide (TiO_2) disposition

Cells	Characteristics of particles and exposure	Exposure protocol	Observed effect(s)	Reference
Sprague-Dawley alveolar macrophage cell line	TiO_2 [size not specified] up to 100 µg/mL	Particles untreated or opsonized with surfactant protein A, artificial bovine surfactant or rat immunoglobulin G	Opsonization with surfactant components resulted in a modest dose-dependent increase in macrophage uptake of particles compared with untreated particles. These ‘inert’ particles presumably phagocytosed via receptors that require neither activation nor opsonization by airway surface fluid components	Stringer & Kobzik (1996)
Sprague-Dawley rat tracheal explants	21-nm TiO_2 (anatase), 120-nm TiO_2 (anatase); 5 mg/mL suspension	Explants submerged epithelial side up; after 1 h, explants removed from suspension and placed in media for 3–7 days	Ultrafine particles appeared to enter epithelial cells more rapidly than fine particles. Results suggested that once ultrafine TiO_2 particles enter epithelial cells they are readily translocated to the interstitium, whereas fine particles tend to remain in the epithelial cells. Both fine and ultrafine particles tended to aggregate, but the aggregates of ultrafine particles were larger and encompassed a greater number of particles. The aggregate size of fine particles decreased over time, while that of ultrafine particle increased over time.	Churg *et al.* (1998)
BALB/C mouse tumour monocytic macrophages, J774.2 cell line	29-nm TiO_2, 250-nm TiO_2, 15.7–125 µg/mL (0.0975–0.78 µg/mm^2)	Cells cultured for 8 h with particles; medium subsequently changed and cells incubated for 24 h with 2-µm latex beads (5:1, bead:cell) to assess phagocytic activity	Phagocytosis was inhibited by all particle types at 125 µg/mL (0.78 µg/mm^2). However, at the lowest dose (0.0975 µg/mm^2) there was a tendency for ultrafine particles to increase phagocytic activity.	Renwick *et al.* (2001)

Table 4.3 (contd)

Cells	Characteristics of particles and exposure	Exposure protocol	Observed effect(s)	Reference
Wistar rat lung macrophages	29-nm TiO_2, 250-nm TiO_2, 125, 500 μg instilled/rat	Particles instilled in male rats 24 h before they were killed and cells collected; cells cultured 18 h with 2-μm latex beads (5:1, bead:macrophage) to assess phagocytic activity	Phagocytic activity was significantly decreased relative to control for macrophages from rats instilled with all particle types/sizes at the 500-μg dose, but was unaffected at the 125-μg dose. At the 500-μg dose, phagocytosis tended to decrease progressively from fine TiO_2 to ultrafine TiO_2. Chemotactic activity of macrophages was significantly increased by ultrafine particles at the 500-μg dose, but was similar to saline control for fine particles and the low dose.	Renwick *et al.* (2004)
Skin from domestic pigs (5 months)	Titanium formulations (T-Lite), 10% TiO_2, needle-line particles of 30–60 nm×10 nm coated with methicone or methicone and silica; 400 μg/cm^2 or 240 μg/cm^2	Test formulations applied for 24 h to 1 cm^2 exposed skin (500 μm thick)	No dermal penetration of TiO_2 wasobserved for the tested suncreen formulations. Applied TiO_2 particles were mostly aggregates up to 200 nm and occasionally up to 1 μm. Virtually all the applied TiO_2 was recovered from skin surface by washing with sponge dipped in soap solution.	Gamer *et al.* (2006)

reported that Long-Evans rats (358 g) relative to smaller Fischer 344 rats (231 g) received a lower normalized total lung dose following a 7-hour exposure to titanium dioxide (0.43 versus 0.52 µg/g bw and 105 versus 114 µg/g lung, respectively).

Bellmann *et al.* (1991) found about 40% greater lung burdens of inhaled titanium dioxide in male Fischer 344 rats compared with similarly exposed female rats. When the mass of titanium dioxide was normalized to lung weight, however, lung burdens were similar between the males and females.

The method of delivery (instillation *versus* inhalation) affects the dose rate of particles delivered to the lungs as well as the distribution of these particles within the lungs and may also potentially affect observed pulmonary responses. The lobe-to-lobe distribution of inhaled titanium dioxide is associated with lobe weight (Ferin & Morehouse, 1980; Osier & Oberdörster, 1997). Osier and Oberdörster (1997) suggested that the increased response following instillation may be due to focal areas of high particle burden, differences in dose rate or clearance kinetics. Driscoll *et al.* (1991) also reported that, for similar lung burdens of titanium dioxide, instillation induced transient increases in levels of lavage protein and polymorphonuclear neutrophils that were not observed following inhalation exposures. Following a 12-week exposure to titanium dioxide, Oberdörster *et al.* (1994, 1997) measured the clearance kinetics of both fine and ultrafine titanium dioxide as well as the clearance of subsequently administered radiolabelled particles (3.3 µm). The method of delivery of this radiolabelled particle, i.e. by inhalation or instillation, did not appear to affect the measured pulmonary clearance rates.

At 25 days after inhalation exposure to a 1.0-µm MMAD titanium-dioxide aerosol, Ferin and Morehouse (1980) reported 70% particle retention in Fischer 344 rats while Long-Evans rats retained only 55%. However, Driscoll *et al.* (1991) only observed 39% retention in Fischer 344 rats 28 days after a 5-day exposure to a 1.0-µm MMAD titanium dioxide aerosol. Pulmonary clearance in rats is also affected by age, with typical retention half-times of 45 days at 5 months versus 74 days at 23 months (Muhle *et al.*, 1990).

The exposure history of animals also affects particle clearance. Exposure to the gaseous pollutants, nitrogen oxide and sulfur dioxide, stimulated particle clearance of titanium dioxide at low levels of exposure but suppressed clearance at higher levels of exposure (Ferin & Leach, 1975). The clearance might be due to macrophages and macrophage recruitment following initial exposure to gaseous pollutants would explain the stimulated clearance. Indeed, the chemotactic activity of macrophages is significantly increased following acute exposures to titanium dioxide (Renwick *et al.*, 2004). However, chronic exposures to high concentrations of titanium dioxide aerosols impaired alveolar clearance to varying degrees in rats and mice (Bermudez *et al.*, 2002, 2004) and possibly in hamsters (Creutzenberg *et al.*, 1998). Co-exposure of rats to cytotoxic aerosols impaired macrophage clearance of titanium dioxide and increased titanium dioxide translocation to the lymph system (Greenspan *et al.*, 1988).

Although differences have been observed between studies, common findings related to the behaviour of titanium dioxide particles in the respiratory tract have been reported. Following subchronic exposures to high concentrations, pulmonary clearance rates of fine titanium-dioxide particles were decreased in both rats and mice and those of ultrafine titanium-dioxide particles were decreased to a greater extent. The evidence in hamsters is contradictory; two studies (Bermudez *et al.*, 2002, 2004) showed no effect of subchronic exposure to titanium dioxide on clearance and one found impaired clearance (Creutzenberg *et al.*, 1998). Rats, mice and hamsters all experienced acute inflammatory responses after exposure to fine and ultrafine titanium-dioxide particles, although the response was greater with ultrafine particles on a mass basis (Bermudez *et al.*, 2002, 2004). Following exposures to titanium dioxide, rats and mice (but not hamsters) also demonstrated increased epithelial permeability which can affect the transport of titanium dioxide and other materials from the lumenal surfaces into the tissues and even the circulation.

Both in-vitro and in-vivo studies have demonstrated the rapid (~1 hour) translocation of free ultrafine-titanium dioxide particles across pulmonary cell membranes (Ferin *et al.*, 1992; Churg *et al.*, 1998; Geiser *et al.*, 2005). Agglomerates of titanium dioxide particles may disassociate once deposited in the lungs; thus, inhaled agglomerate size is the determinant of the amount and site of deposition, but subsequent clearance is influenced by the properties of the agglomerates and the primary particles (Takenaka *et al.*, 1986; Ferin *et al.*, 1992; Bermudez *et al.*, 2002). Following dissociation, ultrafine titanium dioxide particles are cleared more slowly and cause a greater inflammatory response (influx of polymorphonuclear neutrophils) than fine titanium dioxide particles (Ferin *et al.*, 1992; Oberdörster *et al.*, 1994, 2000; Bermudez *et al.*, 2002, 2004). An increase in the transport by macrophages of titanium dioxide to lymph nodes has been reported following inhalation of a cytotoxin (Greenspan *et al.*, 1988). However, Geiser *et al.* (2005) reported that ~80% of 22-nm titanium dioxide particles remained on the lumenal alveolar surface of rats 24 hours after inhalation. Both ultrafine and fine (0.078 and 0.2 μm in diameter) particles cross cellular membranes by non-endocytic (i.e. those that involve vesicle formation) mechanisms such as adhesive interactions and diffusion, whereas the phagocytosis of larger 1-μm particles is ligand receptor-mediated (Geiser *et al.*, 2005). The differences in inflammatory effects and possibly lymph node burdens between fine and ultrafine titanium dioxide appear to be related to lung burden in terms of particle surface area and not particle mass or number (Oberdörster *et al.*, 1992a; Oberdörster 1996; Oberdörster *et al.*, 2000; Tran *et al.*, 2000). The surface properties of titanium dioxide (e.g. roughness) may affect protein binding, and smoother titanium dioxide surfaces are more hydrophobic (Sousa *et al.*, 2004).

The apparent dysfunction in pulmonary clearance as measured by lung burden of titanium dioxide following long-term exposure might not be representative for clearance of subsequently inhaled fine particles (ILSI Risk Science Institute Workshop Participants, 2000). When titanium-dioxide particles are sequestered, they may not necessarily influence nor would their clearance kinetics be reflective of macrophage-mediated removal of subsequently inhaled materials. For example, following a subchronic 12-week exposure, lung burdens of both silica and ultrafine titanium dioxide suggested impaired macrophage clearance (Oberdörster *et al.*, 1994). The prolonged lung burdens were presumed to be due to the cytotoxicity of silica dioxide and sequestration of ultrafine titanium dioxide in the interstitium. However, exposure to radiolabelled polystyrene (3.3 µm) particles also revealed a delay in clearance in animals exposed to both silica and ultrafine titanium dioxide. These large polystyrene particles were probably not sequestered even in the presence of increased epithelial permeability, and thus demonstrated impaired alveolar macrophage-mediated clearance.

4.2.2 *Toxic effects*

(a) In vivo

As reported previously (IARC, 1989), administration of high doses of titanium dioxide to experimental animals by intraperitoneal or intrapleural injection or by intratracheal instillation into the lung resulted in varying degrees of inflammation with minimal associated pathology (lung damage or fibrosis). Some studies demonstrated the fibrotic potential of titanium dioxide in rats (Muhle *et al.*, 1991) in contrast to a wide range of studies that failed to demonstrate any fibrotic potential of fine titanium dioxide in rats or rabbits (IARC, 1989; Ferin & Oberdörster, 1985). However, one study showed that intratracheal instillation of 3 mg titanium dioxide to hamsters once a week for 15 weeks resulted in slight pulmonary inflammation and, subsequently, pathological evidence of interstitial fibrosis (Stenbäck *et al.*, 1976). Normal clearance pathways from the lung were impaired in rats that had been exposed to 250 mg/m^3 rutile for six hours per day on five days per week for two years, and massive accumulation of dust-laden macrophages was observed. In addition, free particles and cellular debris were found in the alveoli, and alveolar proteinosis and cholesterol granulomas developed. Lung weights were increased and white patches of accumulated material were seen in the lungs at necropsy (Lee *et al.*, 1985a,b, 1986). The collective results from these studies are consistent with a breakdown of normal clearance functions and altered lung structure due to the massive amount of titanium dioxide retained. The lowest exposure concentration of 10 mg/m^3 showed minimal effects whereas the 50-mg/m^3 dose also showed evidence of overload. Most of the pathology and related changes were considered by the authors to be overload-dependent.

Several studies have expanded the understanding of the toxicity of titanium dioxide, especially under conditions of lower exposure. Moreover, studies that used ultrafine or nanosize titanium dioxide showed enhanced toxicity relative to the fine particles used in earlier studies (IARC, 1989).

Baggs *et al.* (1997) compared the inhalation toxicity of fine (250 nm) versus ultrafine (20 nm) titanium dioxide (~23 mg/m^3 for six hours per day on five days per week for three months) in male Fischer 344 rats. After six months in clean air following exposure, fine titanium dioxide induced a minor degree of fibrous changes at three months, as shown by trichrome collagen staining, which was less than that in the ultrafine-treated group. The fibrous deposits (indicated by staining) decreased after six months in clean air and then became not significantly greater than those in controls at 12 months. Ultrafine particles were more fibroproliferative in rats than fine titanium dioxide, but the fibrotic lesions (generally thought to be permanent) appeared to be reversible. Earlier work by this group (Ferin & Oberdörster, 1992) showed that inhalation of fine (250 nm) or ultrafine (20 nm) titanium dioxide (~23 mg/m^3 for 6 hours per day on 5 days per week) for 12 weeks induced differential tissue uptake of the particles (most notably at 12 weeks of exposure) and that ultrafine titanium dioxide induced much more and increasing inflammation throughout the 12-week period of exposure. It was concluded that the ultrafine particles had probably passed into the lung epithelium after having escaped phagocytosis. Intratracheal instillation with 500 μg of each type of particle yielded largely analogous findings 1 and 29 days after treatment but inflammation returned to normal at 59 days in both treatment groups.

In related studies that used the same exposures, Oberdörster *et al.* (1992a,b) provided further evidence for heightened inflammation and associated pro-inflammatory mediators in the lungs of rats exposed to ultrafine titanium dioxide as well as for reduced clearance detected by a radiotracer. The impact of the particles on inflammation correlated better with surface area than with dose mass. Osier and Oberdörster (1997) also investigated fine (250 nm) and ultrafine (20 nm) titanium dioxide in a comparative study of intratracheal instillation versus inhalation that allowed an approximation of similar acute (single exposure) lung burdens (500 and 750 μg, respectively). Acute effects (e.g. inflammation) were quantitatively similar until 7 days after exposure and the differential potency was consistent with that previously noted for ultrafine and fine particles. Instillation elicited a greater intensity of response possibly due to differences in dose rate and a less dispersed distribution of particles in the distal lung. Similar results were reported by Renwick *et al.* (2004) but the differences between the size modes that were apparent in male Wistar rats instilled with 500 μg were not evident in those administered 125 μg.

Inhalation studies with fine titanium dioxide have generally been consistent with earlier findings that suggested that its toxicity is similar to that of other poorly soluble particles (ILSI Risk Science Institute Workshop Participants, 2000). Male HAN rats exposed for 3–30 days (on 5 days per week) to 50 mg/m^3 fine titanium dioxide and followed up to 75 days showed little or no evidence of toxicity (Brown *et al.*, 1992). Tests for macrophage chemotaxis with the Boyden chamber at any time after exposure showed no stimulatory effect of titanium dioxide, which was consistent with the general lack of inflammation. A similar 5-day exposure (for 6 hours per day) to titanium dioxide (1 μm) was assessed for profibrotic inflammatory end-points 7–63 days after exposure (Driscoll *et al.*, 1991). Lung burden was 1.8 mg at 5 days and retention was 38.6% 28 days after exposure. Bronchoalveolar lavage indices showed no evidence (cellular, enzyme or cytokine) of damage or inflammation, nor was there evidence of macrophage activation that might lead to fibrosis under the conditions of this study.

Inhalation of 5, 50 and 250 mg/m^3 pigment-grade (fine) titanium dioxide (~1.7 μm) for 6 hours per day on 5 days per week for 4 weeks by male Crl:CDBR rats was evaluated for various inflammation-related end-points at 1 week and 1, 3 and 6 months after exposure (Warheit *et al.*, 1997). Effects consistent with prolonged (but slowly decreasing) inflammation and macrophage impairment were generally limited to the 250-mg/m^3 exposure group (12 mg retained dose). The lower-exposure groups recovered in an inverse dose-dependent manner. Pathology reflected the retained titanium dioxide in aggregated particle-laden macrophages and foamy cells, with no evidence of significant fibrosis.

Instillation of titanium dioxide (200 μg) [size of the dust particles not specified] into female C3H/He mice did not alter the clonal activity of macrophages harvested 40 days after exposure, which would be consistent with the unimpaired health of macrophages and the lack of evidence of profibrotic activity (Oghiso *et al.*, 1992). A much broader array of pulmonary and systemic immunological end-points were evaluated in Fischer 344 rats exposed for 8 consecutive days (~40 mg/m^3; 2.2 μm; σ_g=1.4; 5 hours per day) (Huang *et al.*, 2001). Assays up to 5 months after exposure showed minimal if any impact on associated immune function and cell mediators.

Several studies of subchronic to chronic duration have compared particle sizes and species responses to relatively low levels of titanium dioxide. Henderson *et al.* (1995) exposed female Fischer 344 rats to 0, 0.1, 1.0 and 10 mg/m^3 fine commercial-grade titanium dioxide by inhalation for 4 weeks (6 hours per day on 5 days per week). Lung burdens ranged from 4.4 to 440 μg after 1 week. Other groups of rats received instillations of 50, 200 and 750 μg to parallel these groups; higher doses were used due to the lack of apparent effects of the titanium dioxide. Measurement of cells, enzyme and cytokine markers and pathological lesions showed no effect of titanium throughout the study (1, 8 and 24 weeks after exposure) for either inhalation or instillation exposures.

Bermudez *et al.* (2002, 2004) exposed female rats, mice and hamsters by inhalation to fine (rutile; 250-nm primary particles) and ultrafine (21-nm primary particles) titanium dioxide (see Table 4.1 for details of exposure). In the study of fine titanium dioxide (Bermudez *et al.* 2002), particles accumulated in all species at 10 mg/m^3 and all species cleared the particles substantially during the period after exposure (rats>mice>hamsters), although hamsters cleared particles more completely than mice and mice more completely than rats by 1 year after exposure. At 50 and 250 mg/m^3, mice and rats accumulated more particles than hamsters and both were in overload within a minimal period after exposure in contrast to the nearly complete clearance in hamsters. Bronchoalveolar lavage indices of lung injury and inflammation at the high concentrations showed high neutrophil responses in all species and reversal in rats and mice was retarded (rat > mouse) in comparison with hamsters. Significant inflammation (but to a much much lesser extent than that with the high-level exposures) occurred in rats at 10 mg/m^3. Inflammation markers generally followed this pattern. Rats exposed to concentrations of 50 and 250 mg/m^3 developed a dose-dependent accumulation of dust in the cells, hyperplasia and alveolar lipoproteinosis. Minute collagenized fibrosis occurred in the alveolar walls that enclosed large dust–cell aggregates. The nature of the lesions in rats appeared to be actively fibroproliferative compared with those in mice and hamsters.

Indices of epithelial cell proliferation in the end airways and alveoli were seen primarily in rats and were persistent.

In the study of ultrafine titanium dioxide, Bermudez *et al.* (2004) reported that mice and rats had similar normalized lung burdens but that mice appeared to clear the particles faster than rats, except at 10 mg/m^3 when they were almost identical and appeared to have arrested clearance. In contrast, hamsters exhibited rapid clearance regardless of the exposure level. Bronchoalveolar lavage indices of lung injury and inflammation showed a greater neutrophil response in rats across the ranges of concentrations and mice showed an early high macrophagic response that decreased to below that of rats over time. Pathology (septal thickening and fibrosis) generally followed these patterns (hamsters had virtually none) and the nature of the lesions in rats appeared to be actively fibroproliferative compared with those of mice and hamsters. Indices of epithelial cell proliferation in the end airways were consistent with these observations; the reversal after exposure was most rapid in hamsters.

The impact of surface treatment on the acute lung toxicity of titanium dioxide particles was assessed in a short-term pulmonary assay with Crl:CD(SD)/GS BR rats. The particles used were R-100 titanium dioxide (1 wt% alumina; average size, 300 nm; average surface area, 6 m^2/g) and Pigment A titanium dioxide (1 wt% alumina, 3 wt% amorphous silica encapsulating the particle; average size, 290 nm; average surface area, 7.9 m^2/g), both of which were in the rutile form. Rats received a single dose of 1 or 5 mg/kg bw of the particles dispersed in phosphate buffered saline. Bronchoalveolar lavages were conducted 24 hours, 1 week, 1 month and 3 months after instillation. The inflammatory response to titanium dioxide particles was transient; this may have been the result of the instillation process itself as it was also seen in the vehicle-control group. Similar responses were observed with the lavage fluid parameters (lactate dehydrogenase, microprotein and alkaline phosphatase) and similar results were seen in the rate of lung parenchymal cell proliferation. Histopathological analyses of lung tissues showed no significant adverse effects of titanium dioxide (both types) (Warheit *et al.*, 2005).

A 2-year chronic inhalation study with commercial-grade titanium dioxide (~1.6 μm; 0, 10, 50 and 250 mg/m^3 for 6 hours per day on 5 days per week) demonstrated the transmigration of particles to systemic tissues, notably the liver and spleen (Lee *et al.*, 1985a,b). The authors surmised from the minimal presence of particles not associated with immune or phagocytic cells that the dose-dependent systemic evidence of particles was indicative of transmigration through the lymphatic system into the blood. There was evidence of mild focal fibrosis with few apparent interstitial particles.

Muhle *et al.* (1990, 1991) reported a series of studies that involved exposure of rats and hamsters to rutile and anatase titanium dioxide (5–30 mg/m^3) and described overload and mild inflammation in both species, although the condition appeared to be more severe (based on pathology) in rats. The anatase form was somewhat more potent in rats than the rutile form, which may reflect the 10-fold smaller size of the anatase (0.02–0.04 μm versus 0.2–0.7 μm). Pathological evidence of fibrogenesis was reported in rats.

(b) *In vitro*

Iyer *et al.* (1996) found that primary human macrophages cultured for up to 24 hours with 60 μg/mL commercial-grade titanium dioxide (0.45 μm) did not show apoptosis or any other evidence of DNA damage that might initiate profibrotic inflammation.

Pro-inflammatory pathways that involve IκBα degradation were assessed by examining its linkage to interleukin (IL)-8 expression (Schins *et al.*, 2000) in A549 epithelial cell cultures treated with commercial fine titanium dioxide (40 μg/cm^2). Degradation of IκBα correlated with a brief induction of IL-8 (a pro-inflammatory cytokine) that rapidly decreased; this led the authors to conclude that titanium dioxide has transient but probably minimal inflammatory potential.

In a rat nasal epithelial model that predicts upper respiratory tract toxicity *in vivo* and *in vitro* (Kilgour *et al.*, 2000), nasal turbinates from mice were incubated with titanium dioxide, and adenosine triphosphate was evaluated in the nasal olfactory epithelium or respiratory epithelium. Titanium dioxide caused little or no loss of adenosine triphosphate in either.

The in-vitro toxicity of ultrafine titanium dioxide particles (40 nm) was assessed by cell morphology, mitochondrial function, membrane leakage of lactate dehydrogenase and reduced glutathione levels as well as the release of reactive oxygen species in mitochondrial membrane potential (Hussain *et al.*, 2005). Titanium dioxide was used as a negative control based on published data that ultrafine particles of titanium dioxide show no toxicity to these cells. Titanium dioxide appeared to have the lowest level of toxicity to cells for any of these parameters.

Donaldson and Brown (1988) compared the rutile form of titanium dioxide (medium volume diameter, 2.4 μm) with crocidolite asbestos and quartz. Rat alveolar macrophages released ^{51}Cr (indicative of cell damage) in significantly lower quantities after exposure to titanium dioxide than after exposure to either crocidolite asbestos or quartz.

Yamamoto *et al.* (2004) tested the cytotoxicity of ceramic particles of different sizes and shapes and found that dendritic particles of titanium dioxide had significantly greater toxicity than those that were spherical or spindle shaped.

Human skin fibroblasts preincubated for 18 hours with 10 μg/cm^2 titanium dioxide (anatase, 450 nm) and then irradiated with UVA showed dose-dependent photocytoxicity, which suggested that nucleic acids are a potential target for photo-oxidative damage that has been sensitized with titanium dioxide (Wamer *et al.*, 1997).

Stringer and Kobzik (1998) evaluated the effect of titanium dioxide in increasing IL-8 production in primed A549 human lung epithelial cells and found that it caused significantly less tumour necrosis factor -α and IL-8 release than residual oil fly ash or pathogenic α-quartz dust. Using a mouse macrophage cell line, Thibodeau *et al.* (2003) found that exposure to α-quartz silica elicited activation of caspase 3 and caspase 9, whereas exposure to titanium dioxide did not.

Exposure of mouse peritoneal macrophages *in vitro* to 100 μg/mL titanium dioxide in the culture medium was found to inhibit the phagocytic activity of cells compared with controls (Nuuja & Arstila, 1982). The phagocytosis of alveolar macrophages was impaired following exposure to ultrafine particles including titanium dioxide (Renwick *et al.*, 2001). Oberdörster *et al.* (1992a) found that alveolar macrophages exposed to ultrafine titanium dioxide (12 and 20 nm diameter) have a greater potential to induce cytokines than those exposed to larger-sized particles.

Li (1986) and Li and Myers (1988) found that titanium dioxide caused significantly less damage than chrysotile or calcite fibres in airway epithelial cells using an in-vitro lung epithelial cell system for evaluating the potential toxicity of inhalable material. Titanium dioxide was far less toxic than calcium sulfate, chrysotile crocidolite and phosphate fibres.

4.2.3 *Genetic and related effects*

Investigations on the genetic and related effects of titanium dioxide have been performed using isolated DNA and cell culture-based test systems, as well as animals. In several of these studies titanium dioxide was used as a negative control. Other studies have evaluated the toxic properties of titanium dioxide in relation to its size (e.g. fine versus ultrafine) and/or chemistry (e.g. anatase versus rutile). Several studies have also addressed the photosensitization effects of titanium dioxide. In view of the contrasting photocatalytic and biological activities of titanium dioxide in relation to size and chemical composition (Oberdörster *et al.*, 2005), specifications of each sample tested are provided whenever available.

(a) Isolated DNA

Unwinding and breakage of plasmid DNA *in vitro* has been used to investigate the generation of reactive oxygen species by various mineral dusts including titanium dioxide (Donaldson *et al.*, 1996). [The Working Group noted the limited relevance of this assay for assessing particle-induced genetic damage]. A comparison of fine (500 nm) *versus* ultrafine (20 nm) titanium dioxide using ΦX174 RF plasmid DNA showed markedly stronger strand breakage for the ultrafine sample. DNA damage by the ultrafine titanium dioxide was prevented by the presence of mannitol, which suggests that the damaging effects were due to hydroxyl radicals (Donaldson *et al.*, 1996). In contrast, in a more recent study, ultrafine titanium dioxide (20 nm; 49.8 m^2/g) failed to damage ΦX174 RF DNA unlike various other particles of similar size (Dick *et al.*, 2003). [Different incubation times as well as different relative amounts of plasmid DNA and titanium dioxide were used in the two studies.]

The effects of UV light-irradiated titanium dioxide on isolated DNA have been investigated. Upon co-exposure with simulated sunlight (300–400 nm), both the anatase and rutile forms [particle size not specified] of titanium dioxide induced damage in pBluescript II SK^+ plasmid DNA; anatase showed stronger effects than rutile (Dunford *et al.*, 1997). Photo-irradiated (365 nm; UVA) anatase and rutile (size range, 50–300 nm) also caused the formation of 8-hydroxy-2′-deoxyguanosine in calf thymus DNA in the presence of copper chloride (Hirakawa *et al.*, 2004). Again, anatase showed stronger effects than rutile. In the absence of irradiation, no DNA damage was found. Following irradiation, both samples also showed enhanced formamidopyrimidine glycosylase-mediated cleavage of DNA fragments that contained human tumour-suppressor genes *P53* and *P16* and the c-Ha-*RAS*-1 oncogene (Hirakawa *et al.*, 2004). Oxidative damage in calf thymus DNA was also reported after combined treatment with UVA (320–400 nm) and titanium dioxide (average size, 450 nm) (Wamer *et al.*, 1997).

(b) Cellular effects (for details and references, see Table 4.4)

Anatase titanium dioxide (21 nm) was not mutagenic to *Salmonella typhimurium* TA100, TA98 or TA102. Titanium dioxide [unspecified] did not induce somatic mutation or recombination in *Drosophila melanogaster.*

Anatase (255 nm) but not 21-nm anatase or rutile (255 or 420 nm) titanium dioxide caused DNA strand breaks in mouse lymphoma L5178Y cells. Induction of oxidative DNA damage (8-hydroxy-2′-deoxyguanosine formation) was seen in rat lung epithelial cells treated with 180-nm anatase titanium dioxide. Anatase titanium dioxide did not enhance unscheduled DNA synthesis in rat pleural mesothelial cells or induce mutation in mouse lymphoma L5178Y/tk$^{+/-}$ or RLE-6TN rat lung epithelial cells.

Titanium dioxide caused a dose-dependent increase in sister chromatid exchange in Chinese hamster CHO-K1 cells at non-toxic concentrations but not in rat pleural mesothelial or Chinese hamster ovary CHO cells. No micronucleus formation was found in Chinese hamster ovary CHO cells incubated with titanium dioxide either in the presence or absence of metabolic activation. In contrast, titanium dioxide did induce micronuclei in Chinese hamster CHO-K1 cells. Titanium dioxide samples of different size or chemistry did not cause micronucleus formation in RLE rat liver epithelial cells, but a sample of ultrafine (≤20 nm) titanium dioxide did induce micronuclei in Syrian hamster fibroblasts, while >200-nm titanium dioxide was inactive. The ultrafine sample also elicited apoptosis in these cells. Titanium dioxide did not include chromosomal aberrations in Chinese hamster CHU/IU cells (21-nm anatase), Chinese hamster CHO cells or rat pleural mesothelial cells (anatase [size unspecified]). Titanium dioxide did not cause cell transformation of Syrian hamster embryo or mouse BALB/3T3/31–1-1 cells.

Enhanced oxidative DNA damage was observed in BEAS-2B human bronchial epithelial cells with 10-nm and 20-nm anatase and 200-nm rutile. A 1:1 mixture of 200-nm anatase and 200-nm rutile caused stronger oxidative DNA damage than either of these alone. No oxidative DNA damage was observed in CRL human skin fibroblasts [unspecified titanium dioxide]. DNA strand breakage assays (alkaline unwinding) in WI-26 human embryonal lung cells showed negligible effects of titanium dioxide [unspecified]. The compound did not induce mitochondrial dysfunction (i.e. membrane potential change) in A549 human lung epithelial cells. In BEAS-2B human bronchial epithelial cells, micronucleus formation was induced with 10-nm and 200-nm anatase titanium dioxide (not with >200-nm anatase or 200-nm rutile). Increased multinucleation was found in Met-5A human mesothelial cells treated with titanium dioxide [unspecified], but no such effect was observed in primary human mesothelial cells.

Table 4.4. Genetic and related effects of titanium dioxide

Test system	Result[a]		Dose[b] (LED/HID)	Reference
	Without exogenous metabolic system	With exogenous metabolic system		
Salmonella typhimurium TA100, TA102, TA98, reverse mutation	–	NT	40 000 µg/mL (21-nm anatase)	Nakagawa *et al.* (1997)
Drosophila melanogaster, wing mosaic assay	–		300 mM[c]	Tripathy *et al.* (1990)
DNA strand breaks (comet asssay), mouse lymphoma L5178Y/tk$^{+/-}$ cells *in vitro*	+	NT	800 µg/mL (255-nm anatase)	Nakagawa *et al.* (1997)
DNA strand breaks (comet assay), mouse lymphoma L5178Y/tk$^{+/-}$ cells *in vitro*	–	NT	3200 µg/mL (255-nm rutile; 420-nm rutile); 800 µg/mL (21-nm anatase)	Nakagawa *et al.* (1997)
Oxidative DNA damage, RLE rat lung epithelial cells *in vitro*	+	NT	1700 µg/mL	van Maanen *et al.* (1999)
Unscheduled DNA synthesis, rat pleural mesothelial cells *in vitro*	–	NT	50 µg/mL (anatase) (10 µg/cm^2)[d]	Endo-Capron *et al.* (1993)
Gene mutation, L5178Y/tk$^{+/-}$ mouse lymphoma cells *in vitro*	–	NT	2000 µg/mL (21-nm anatase)	Nakagawa *et al.* (1997)
Gene mutation, *Hprt* locus, RLE-6TN rat lung epithelial cells *in vitro*	–	NT	100 µg/cm^2 (180-nm anatase)	Driscoll *et al.* (1997)
Sister chromatid exchange, Chinese hamster CHO-K1 cells *in vitro*	+	NT	1 µM[c]	Lu *et al.* (1998)
Sister chromatid exchange, Chinese hamster ovary CHO cells *in vitro*	–	–	25 µg/mL	Ivett *et al.* (1989)
Sister chromatid exchange, RLE rat pleural mesothelial cells *in vitro*	–	NT	37.5 µg/mL (5 µg/cm^2)	Endo-Capron *et al.* (1993)
Micronucleus formation, Chinese hamster CHO-K1 cells *in vitro*	+	NT	2 µM[c]	Lu *et al.* (1998)

Table 4.4 (contd)

Test system	Result[a]		Dose[b] (LED/HID)	Reference
	Without exogenous metabolic system	With exogenous metabolic system		
Micronucleus formation, Chinese hamster CHO cells *in vitro*	–	–	10 µg/mL	Miller *et al.* (1995)
Micronucleus formation, RLE rat liver epithelial cells *in vitro*	–	NT	20 µg/cm^2 (20-nm anatase; 170-nm rutile)	Linnainmaa *et al.* (1997)
Micronucleus formation, Syrian hamster embryo cells *in vitro*	+	NT	1 µg/cm^2 (ultrafine ≤20 nm)	Rahman *et al.* (2002)
Micronucleus formation, Syrian hamster embryo cells *in vitro*	–	NT	10 µg/cm^2 (fine[e] >200 nm)	Rahman *et al.* (2002)
Chromosomal aberrations, Chinese hamster ovary CHO cells *in vitro*	–	–	25 µg/mL	Ivett *et al.* (1989)
Chromosomal aberrations, Chinese hamster CHU/IU cells *in vitro*	–	NT	800 µg/mL (21-nm anatase)	Nakagawa *et al.* (1997)
Chromosomal aberrations, rat pleural mesothelial cells *in vitro*	–	NT	10 µg/cm^2 (anatase)	Yegles *et al.* (1993)
Cell transformation, BALB/3T3/A31-1-1 mouse cells	–	NT	100 µg/cm^2 (anatase; rutile)	Saffiotti & Ahmed (1995–1996)
Cell transformation, Syrian hamster embryo cells	–	NT	75 µg/mL	LeBoeuf *et al.* (1996)
DNA strand breaks (alkaline unwinding), WI-26 human embryonal lung cells *in vitro*	–	NT	500 µg/mL	Kamp *et al.* (1995)
Oxidative DNA damage, CRL1634 human skin fibroblasts *in vitro*	–	NT	71.4 µg/mL (10 µg/cm^2)	Wamer *et al.* (1997)
Oxidative DNA damage (FPg-comet assay), human BEAS-2B bronchial epithelial cells *in vitro*	+	NT	10 µg/mL (1.77 µg/cm^2) 10-nm anatase, 20-nm anatase, 200-nm rutile	Gurr *et al.* (2005)

Table 4.4 (contd)

Test system	Result[a]		Dose[b] (LED/HID)	Reference
	Without exogenous metabolic system	With exogenous metabolic system		
Micronucleus formation, Met-5A human mesothelial cell line *in vitro*	+	NT	2 μg/cm^2 [unspecified]	Pelin *et al.* (1995)
Micronucleus formation, primary human mesothelial cells *in vitro*	–	NT	5 μg/cm^2 [unspecified]	Pelin *et al.* (1995)
Micronucleus formation, human BEAS-2B bronchial epithelial cells *in vitro*	–	NT	10 μg/mL (1.77 μg/cm^2) 200-nm rutile, >200-nm anatase	Gurr *et al.* (2005)
Micronucleus formation, human BEAS-2B bronchial epithelial cells *in vitro*	+	NT	10 μg/mL (1.77 μg/cm^2) 10-nm anatase, 200-nm anatase,	Gurr *et al.* (2005)
Oxidative DNA damage, rat lung *in vivo*	–		2×50 mg/kg it (180 nm anatase)	Driscoll *et al.* (1997)
Gene mutation, *Hprt* locus, rat alveolar epithelial cells *in vivo*	+		100 mg/kg it (180 nm anatase)	Driscoll *et al.* (1997)
Micronucleus formation, mouse bone-marrow cells, peripheral blood lymphocytes *in vivo*	+		1000 mg/kg, ip×3	Shelby *et al.* (1993)

[a] +, positive; –, negative; NT, not tested;

[b] HID, higher inhibitory dose; LED, lower efficient dose, in-vitro tests, μg/mL; in-vivo tests, mg/kg bw; ip, intraperitoneal; it, intratracheal

[c] Dose expressed in molarity

[d] One of three experiments was positive.

[e] Dose for fine sample not specified in detail [‘similar’ concentrations were used for fine and ultrafine]

(c) *Cellular effects in combination with UV irradiation*

In relation to its application in sunscreens or its photocatalytic activity, several studies have addressed the effects photo-irradiated titanium dioxide. Micronucleus formation was not enhanced in rat liver epithelial cells after treatment with 170-nm anatase, 20-nm anatase or 20-nm aluminium hydroxide/stearic acid-coated rutile in combination with irradiation with UVA (at 365 nm wavelength) (Linnainmaa *et al.*, 1997). In contrast, irradiated (300–400 nm wavelength) MRC-5-fibroblasts showed increased DNA strand breakage in the presence of anatase or rutile [sizes not specified] compared with cells irradiated in the absence of titanium dioxide (Dunford *et al.* 1997). In human skin fibroblasts (CRL1634, ATCC), enhanced oxidation of RNA was observed following combined titanium dioxide (particle size, 450 nm) plus UVA (320–400 nm). Treatment with titanium dioxide plus UVA did not cause increased oxidative damage to DNA (Wamer *et al.*, 1997). Four titanium dioxide samples, i.e. a 21-nm anatase, a 255-nm anatase, a 255-nm rutile and a 420-nm rutile, were tested in an assay that measured DNA strand breakage in L5178Y/tk$^{+/-}$ mouse lymphoma cells. In the presence of UV light, all samples induced enhanced DNA strand breakage as determined by the alkaline comet assay at concentrations that also caused cell death (Nakagawa *et al.*, 1997). In the same study, the 21-nm anatase sample induced chromosomal aberrations in the Chinese hamster CHL/IU cell line in the presence but not in the absence of UV/visible light. Besides polyploidy, the principal structural aberrations that occurred after treatment with 21-nm titanium dioxide plus UV light were chromatid breaks and chromatid exchanges, which occurred at cytotoxic concentrations (Nakagawa *et al.*, 1997). The same sample was not mutagenic in *S. typhimurium* strains TA100, TAS98 or TA102, or when tested in an L5178Y/tk$^{+/-}$ colony formation assay when irradiated with UV light (Nakagawa *et al.*, 1997).

(d) *Studies in rodents (see also Table 4.4)*

The induction of oxidative DNA damage in rat lungs was investigated after intratracheal instillation with two different samples of titanium dioxide, i.e. an untreated titanium dioxide (P-25, hydrophilic surface) and a trimethoxyoctylsilane-treated titanium dioxide (T-805, silanised/hydrophobic surface; particle size, ~20 nm). Transmission electron microscopy demonstrated a highly aggregated state of both titanium dioxide samples. Oxidative damage, as determined at 90 days in lung sections using 8-oxoguanine antibody, was not enhanced by untreated or silanised titanium dioxide (Rehn *et al.*, 2003).

In-vivo mutagenesis of titanium dioxide (anatase; 180 nm median diameter; 8.8 m^2/g) was studied by *Hprt* analysis of epithelial cells isolated from the lungs of female SPF F344 Fischer rats 15 months after intratracheal instillation. Enhanced *Hprt* mutagenesis was observed with 100 mg/kg bw, a dose that also elicited persistent lung inflammation. The authors suggested that the in-vivo mutagenesis was driven by inflammation (Driscoll *et al.*, 1997).

Intraperitoneal injection of titanium dioxide into mice resulted in enhanced micronucleus formation in bone-marrow cells and peripheral blood lymphocytes. No dose-dependent effect was observed over the range of 200–1000 mg/kg bw (Shelby *et al.*, 1993).

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5. Summary of Data Reported

5.1 Exposure data

Titanium dioxide was first produced commercially in 1923, primarily for pigment production. Relatively small quantities of titanium dioxide are used for non-pigmentary purposes. In 2004, worldwide production of titanium dioxide was 4.4 million tonnes.

Titanium dioxide is obtained from a variety of ores that contain ilmenite, rutile, anatase and leucoxene, which are mined from deposits located throughout the world. Most titanium dioxide pigment is produced from titanium mineral concentrates by the chloride or sulfate process, either as the rutile or the anatase form. The primary particles are typically between 0.2 and 0.3 µm in diameter, although larger aggregates and agglomerates are formed. Ultrafine grades of titanium dioxide have a primary particle size of 10–50 nm and are used predominantly as ultraviolet blockers in sunscreens and plastics, and in catalysts. Most commercial titanium dioxide products are coated with inorganic (e.g. alumina, zirconia, silica) and organic (e.g. polyols, esters, siloxanes, silanes) compounds to control and improve surface properties.

Levels of occupational exposure to titanium dioxide during its manufacture have been reported from the USA and Europe between 1970 and 2000. The highest levels of exposure were observed during packing and milling, although high peak exposure also occurred in occupations such as site cleaning and maintenance. Average levels of exposure to respirable dust in these occupations up to 6 mg/m^3 (geometric mean) were reported, but have declined over time. No data were available that would allow the characterization or quantification of exposure to ultrafine primary particles. Workers in the titanium dioxide manufacturing industry may also be exposed to ore and other dusts, strong acids and asbestos.

Exposure to titanium dioxide in user industries is difficult to estimate and characterize due to the paucity of data. Exposure levels are assumed to be low in the user industries, with the possible exception of workers who handle large quantities of titanium dioxide. No significant exposure to titanium dioxide is thought to occur during the use of products in which titanium dioxide is bound to other materials, such as in paints.

5.2 Human carcinogenicity data

Three epidemiological cohort studies and one population-based case–control study from North America and western Europe were available for evaluation.

The largest of the cohort studies was among white male production workers in the titanium dioxide industry in six European countries. The study indicated a slightly increased risk for lung cancer compared with the general population. However, there was no evidence of an exposure–response relationship within the cohort. No increase in the mortality rates for kidney cancer was found when the cohort was compared with the general population, but there was a suggestion of an exposure–response relationship in internal analyses. The other cohort studies, both of which were conducted in the USA, did not report an increased risk for lung cancer or cancer at any other site; no results for kidney cancer were reported, presumably because there were few cases.

One population-based case–control study conducted in Montréal did not indicate an increased risk for lung or kidney cancer.

In summary, the studies do not suggest an association between occupational exposure to titanium dioxide as it occurred in recent decades in western Europe and North America and risk for cancer.

All the studies had methodological limitations; misclassification of exposure could not be ruled out. None of the studies was designed to assess the impact of particle size (fine or ultrafine) or the potential effect of the coating compounds on the risk for lung cancer.

5.3 Animal carcinogenicity data

Pigmentary and ultrafine titanium dioxide were tested for carcinogenicity by oral administration in mice and rats, by inhalation exposure in rats and female mice, by intratracheal administration in hamsters and female rats and mice, by subcutaneous injection in rats and by intraperitoneal administration in male mice and female rats.

In one inhalation study, the incidence of benign and malignant lung tumours was increased in female rats. In another inhalation study, the incidence of benign lung tumours was increased in the high-dose groups of male and female rats. Cystic keratinizing lesions that were diagnosed as squamous-cell carcinomas but re-evaluated as non-neoplastic pulmonary keratinizing cysts were also observed in the high-dose groups of female rats. Two inhalation studies in rats and one in female mice gave negative results.

Intratracheally instilled female rats showed an increased incidence of both benign and malignant lung tumours following treatment with two types of titanium dioxide. Tumour incidence was not increased in intratracheally instilled hamsters and female mice.

Oral, subcutaneous and intraperitoneal administration did not produce a significant increase in the frequency of any type of tumour in mice or rats.

5.4 Mechanistic considerations and other relevant data

Humans can be exposed to titanium dioxide via inhalation, ingestion or dermal contact. In human lungs, the clearance kinetics of titanium dioxide is poorly characterized relative to that in experimental animals. (General particle characteristics and host factors that are considered to affect deposition and retention patterns of inhaled, poorly soluble particles such as titanium dioxide are summarized in the monograph on carbon black.) With regard to inhaled titanium dioxide, human data are mainly available from case reports that showed deposits of titanium dioxide in lung tissue as well as in lymph nodes.

A single clinical study of oral ingestion of fine titanium dioxide showed particle size-dependent absorption by the gastrointestinal tract and large interindividual variations in blood levels of titanium dioxide. Studies on the application of sunscreens containing ultrafine titanium dioxide to the healthy skin of human volunteers revealed that titanium dioxide particles only penetrate into the outermost layers of the stratum corneum, suggesting that healthy skin is an effective barrier to titanium dioxide. No studies on the penetration of titanium dioxide in compromised skin were available.

Respiratory effects that have been observed among groups of titanium dioxide-exposed workers include a decline in lung function, pleural disease with plaques and pleural thickening, and mild fibrotic changes. However, the workers in these studies were also exposed to asbestos and/or silica.

No data were available on the genotoxic effects in titanium dioxide-exposed humans.

Many data on deposition, retention and clearance of titanium dioxide in experimental animals are available for the inhalation route. Titanium dioxide inhalation studies showed differences—both for normalized pulmonary burden (deposited mass per dry lung, mass per body weight) and clearance kinetics—among rodent species including rats of different size, age and strain. Clearance of titanium dioxide is also affected by pre-exposure to gaseous pollutants or co-exposure to cytotoxic aerosols. Differences in dose rate or clearance kinetics and the appearance of focal areas of high particle burden have been implicated in the higher toxic and inflammatory lung responses to intratracheally instilled versus inhaled titanium dioxide particles. Experimental studies with titanium dioxide have demonstrated that rodents experience dose-dependent impairment of alveolar macrophage-mediated clearance. Ultrafine primary particles of titanium dioxide are cleared more slowly than their fine counterparts.

Titanium dioxide causes varying degrees of inflammation and associated pulmonary effects including lung epithelial cell injury, cholesterol granulomas and fibrosis. Rodents experience stronger pulmonary effects after exposure to ultrafine titanium dioxide particles compared with fine particles on a mass basis. These differences are related to lung burden in terms of particle surface area, and are considered to result from impaired phagocytosis and sequestration of ultrafine particles into the interstitium.

Fine titanium dioxide particles show minimal cytotoxicity and inflammatory/profibrotic mediator release from primary human alveolar macrophages *in vitro* compared with other particles. Ultrafine titanium dioxide particles inhibit phagocytosis of alveolar macrophages *in vitro* at mass dose concentrations at which this effect does not occur with fine titanium dioxide.

In-vitro studies with fine and ultrafine titanium dioxide and purified DNA show induction of DNA damage that is suggestive of the generation of reactive oxygen species by both particle types. This effect is stronger for ultrafine than for fine titanium dioxide, and is markedly enhanced by exposure to simulated sunlight/ultraviolet light.

In-vivo studies have shown enhanced micronucleus formation in bone marrow and peripheral blood lymphocytes of intraperitoneally instilled mice. Increased *Hprt* mutations were seen in lung epithelial cells isolated from titanium dioxide-instilled rats. In another study, no enhanced oxidative DNA damage was observed in lung tissues of rats that were intratracheally instilled with titanium dioxide.

Most in-vitro genotoxicity studies with titanium dioxide gave negative results.

6. Evaluation and Rationale

6.1 Cancer in humans

There is *inadequate evidence* in humans for the carcinogenicity of titanium dioxide.

6.2 Cancer in experimental animals

There is *sufficient evidence* in experimental animals for the carcinogenicity of titanium dioxide.

6.3 Overall evaluation

Titanium dioxide is *possibly carcinogenic to humans (Group 2B).*

6.4 Rationale

In making this evaluation the Working Group considered the human and animal evidence as well as the evidence regarding potential mechanisms through which titanium dioxide might cause cancer in humans.

The Working Group found little evidence of an increased risk for cancer among humans based on epidemiological data, although relatively few studies were available. The single most informative study was a multicountry study of titanium dioxide production workers that found a slightly increased risk for lung cancer compared with the general population and a suggestive dose–response, but no overall excess risk for kidney cancer. The two other cohort studies reported no increased risks and evidence from the case–control study did not indicate an increased risk for either lung or kidney cancer. Overall, these results led the Working Group to conclude that there was *inadequate evidence* from epidemiological studies to assess whether titanium dioxide causes cancer in humans.

In two studies of rats that inhaled titanium dioxide, one observed an excess incidence of lung tumours in both sexes and another in females only. Studies of rats exposed intratracheally found increases in the incidence of lung tumours. No increases were observed among mice and hamsters exposed intratracheally. Other studies that used different routes of administration did not observe excesses in tumour incidence. On the basis of the results of an increased incidence of lung tumours in rats, the Working Group concluded that there was *sufficient evidence* that titanium dioxide is carcinogenic in experimental animals.

The Working Group considered the body of evidence regarding the pathways and mechanisms by which titanium dioxide or other poorly soluble particles may cause cancer. Following the same line of reasoning as that for the other particles reviewed in this volume, the Working Group considered that the available mechanistic evidence for titanium dioxide was not strong enough to warrant a classification other than Group 2B.

Enclosure #6

DuPont Material Safety Data Sheet for Titanium Dioxide (Ti-Pure®) Paint Coatings and Plastics Product Grades

HMIS

Health	:	1
Flammability	:	0
Reactivity/Physical hazard	:	0
PPE	:	Personal Protection rating to be supplied by user depending on use conditions.

Restrictions for use : Ti-Pure® products may not be directly added to food or pharmaceuticals and are not recommended for use in medical devices or cosmetics.

Do not use DuPont materials in medical applications involving implantation in the human body or contact with internal body fluids or tissues unless the material has been provided from DuPont under a written contract that is consistent with DuPont policy regarding medical applications and expressly acknowledges the contemplated use. For further information, please contact your DuPont representative. You may also request a copy of the DuPont POLICY Regarding Medical Applications H-50103-3 and DuPont CAUTION Regarding Medical Applications H-50102-3.

Ti-Pure® is a Registered Trademark of E. I. du Pont de Nemours and Company.

For specific information on composition and properties, see DuPont™ Ti-Pure® Titanium Dioxide Pigment literature. Please see www2.dupont.com/Titanium_Technologies/en_US/ for the latest version of this MSDS.

Contact person : MSDS Coordinator DuPont Titanium Technologies; Wilmington, DE 19898; Telephone (800) 441-9485

The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text.

Significant change from previous version is denoted with a double bar.

SECTION 14. TRANSPORT INFORMATION

Not regulated in transportation by DOT/IMO/IATA.

SECTION 15. REGULATORY INFORMATION

EINECS Status	: On the inventory, or in compliance with the inventory
TSCA Status	: On the inventory, or in compliance with the inventory
AICS Status	: On the inventory, or in compliance with the inventory
DSL Status	: On the inventory, or in compliance with the inventory
ENCS (JP) Status	: On the inventory, or in compliance with the inventory
KECI (KR) Status	: On the inventory, or in compliance with the inventory
PICCS (PH) Status	: On the inventory, or in compliance with the inventory
INV (CN) Status	: On the inventory, or in compliance with the inventory
SARA 313 Regulated Chemical(s)	: SARA 313: This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.
California Prop. 65	: WARNING! This product contains a chemical known to the State of California to cause cancer.The listing of titanium dioxide is for "airborne, unbound particles of respirable size." The listing is not applicable to titanium dioxide when it remains bound within a product matrix.
PA Right to Know Regulated Chemical(s)	: Substances on the Pennsylvania Hazardous Substances List present at a concentration of 1% or more (0.01% for Special Hazardous Substances): Titanium dioxide , Silicon dioxide, amorphous
NJ Right to Know Regulated Chemical(s)	: Substances on the New Jersey Workplace Hazardous Substance List present at a concentration of 1% or more (0.1% for substances identified as carcinogens, mutagens or teratogens): Titanium dioxide , Silicon dioxide, amorphous

SECTION 16. OTHER INFORMATION

pertaining to Group 2B: "possibly carcinogenic to humans", based upon inadequate evidence in humans and sufficient evidence in experimental animals for the carcinogenicity of titanium dioxide. IARC evaluation guidelines consider the generation of tumours, in 2 different studies within the same animal species, to be adequate criteria for an assessment of sufficient evidence.

The conclusions of several epidemiology studies on more than 20000 TiO2 industry workers in Europe and the USA did not suggest a carcinogenic effect of TiO2 dust on the human lung. Mortality from other chronic diseases, including other respiratory diseases, was also not associated with exposure to TiO2 dust.

Based upon all available study results, DuPont scientists conclude that titanium dioxide will not cause lung cancer or chronic respiratory diseases in humans at concentrations experienced in the workplace.

Mutagenicity : Did not cause genetic damage in animals.
Tests on bacterial or mammalian cell cultures did not show mutagenic effects.

SECTION 12. ECOLOGICAL INFORMATION

Aquatic Toxicity

DuPont™ Ti-Pure® Titanium Dioxide Pigment - Paint Coatings - Dry Grades

96 h LC50 : Pimephales promelas (fathead minnow) > 1,000 mg/l

72 h EC50 : Pseudokirchneriella subcapitata (green algae) 61 mg/l

48 h EC50 : Daphnia magna (Water flea) > 1,000 mg/l

SECTION 13. DISPOSAL CONSIDERATIONS

Waste Disposal : Dispose of in accordance with local regulations.

Incompatibility	: None.

SECTION 11. TOXICOLOGICAL INFORMATION

DuPont™ Ti-Pure® Titanium Dioxide Pigment - Paint Coatings - Dry Grades

Inhalation 4 h LC50	: > 6.82 mg/l , rat
Oral LD50	: > 5,000 mg/kg , rat
Skin irritation	: Slight or no skin irritation, rabbit
Eye irritation	: Slight or no eye irritation, rabbit
Sensitisation	: Did not cause sensitization on laboratory animals., mouse Did not cause sensitization on laboratory animals., guinea pig
Repeated dose toxicity	: Oral rat No toxicologically significant effects were found. Inhalation rat No toxicologically significant effects were found.
Carcinogenicity	: In lifetime inhalation studies rats were exposed for 2 years to respectively 10, 50 and 250 mg/m3 of respirable TiO2. Slight lung fibrosis was observed at 50 and 250 mg/m3 levels. Microscopic lung tumours were also observed in 13 percent of the rats exposed to 250 mg/m3, an exposure level that caused lung overloading and impairment of rat lungs clearance mechanisms. In further studies, these tumours were found to occur only under particle overload conditions in a uniquely sensitive species, the rat, and have little or no relevance for humans. The pulmonary inflammatory response to TiO2 particles exposure was also found to be much more severe in rats than in other rodent species. In February 2006, IARC has re-evaluated Titanium dioxide as

use appropriate certified respirators.

Hand protection : Additional protection: Gloves

Eye protection : Safety glasses with side-shields

Exposure Guidelines
Exposure Limit Values

Titanium dioxide				
PEL:	(OSHA)	15 mg/m3	8 hr. TWA	Total dust.
TLV	(ACGIH)	10 mg/m3	TWA	
AEL *	(DUPONT)	10 mg/m3	8 & 12 hr. TWA	Total dust.
AEL *	(DUPONT)	5 mg/m3	8 & 12 hr. TWA	Respirable dust.

* AEL is DuPont's Acceptable Exposure Limit. Where governmentally imposed occupational exposure limits which are lower than the AEL are in effect, such limits shall take precedence.

SECTION 9. PHYSICAL AND CHEMICAL PROPERTIES

Form : crystalline
Color : white
Odor : odourless
pH : not applicable
% Volatile : 0 %
Specific gravity : 3.4 - 4.3
Water solubility : insoluble

SECTION 10. STABILITY AND REACTIVITY

Stability : Stable

SECTION 6. ACCIDENTAL RELEASE MEASURES

NOTE: Review FIRE FIGHTING MEASURES and HANDLING (PERSONNEL) sections before proceeding with clean-up. Use appropriate PERSONAL PROTECTIVE EQUIPMENT during clean-up.

Safeguards (Personnel) : Avoid breathing dust.

Spill Cleanup : Pick up and arrange disposal without creating dust. After cleaning, flush away traces with water.

Accidental Release Measures : Do not flush into surface water or sanitary sewer system.

SECTION 7. HANDLING AND STORAGE

Handling (Personnel) : Avoid breathing dust.
In the manufacture of titanium dioxide, product is packaged at temperatures of approximately 100 to 120 C (212 to 248 F). When pigment is shipped shortly after manufacture, it may stay hot for a very long time depending on ambient temperatures and inventory storage practices. Use caution while handling hot pigment to prevent burns to personnel. Use caution in solvent applications to prevent ignition of solvent.
Wash hands before breaks and at the end of workday.

Handling (Physical Aspects) : This is a fully oxidized mineral product. As such it cannot support combustion or participate in a dust explosion.

Storage : Keep container tightly closed in a dry and well-ventilated place.

SECTION 8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls : Use sufficient ventilation to keep employee exposure below recommended limits.

Personal protective equipment
Respiratory protection : When workers are facing concentrations above the exposure limit they must

Component	CAS-No.	Concentration
Titanium dioxide	13463-67-7	80 - 98 %
Aluminum hydroxide	21645-51-2	0 - 9 %
Silicon dioxide, amorphous	7631-86-9	0 - 11 %

SECTION 4. FIRST AID MEASURES

Skin contact : Wash off with soap and water.

Eye contact : Rinse with plenty of water.

Inhalation : Remove person to fresh air. If signs/symptoms continue, get medical attention.

Ingestion : No specific intervention is indicated. Consult a physician if necessary.

SECTION 5. FIREFIGHTING MEASURES

Flammable Properties
Flash point : does not flash

Suitable extinguishing media : Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.

Firefighting Instructions : The product itself does not burn.

Material Safety Data Sheet

DuPont™ Ti-Pure® Titanium Dioxide Pigment - Paint Coatings - Dry Grades

Version 4.1

Revision Date 11/05/2012 Ref. 150000002071

This SDS adheres to the standards and regulatory requirements of the United States and may not meet the regulatory requirements in other countries.

SECTION 1. PRODUCT AND COMPANY IDENTIFICATION

Product name	:	DuPont™ Ti-Pure® Titanium Dioxide Pigment - Paint Coatings - Dry Grades
Product Grade/Type	:	R-706, R-900, R-902+, R-931, R-960, TS-6200
MSDS Number	:	150000002071
Product Use	:	Colouring agents, pigments
Manufacturer	:	DuPont 1007 Market Street Wilmington, DE 19898
Product Information	:	1-302-774-1000
Medical Emergency	:	1-800-441-3637 (outside the U.S. 1-302-774-1139)
Transport Emergency	:	CHEMTREC: 1-800-424-9300 (outside the U.S. 1-703-527-3887)

SECTION 2. HAZARDS IDENTIFICATION

Potential Health Effects

Skin	:	Contact with dust can cause mechanical irritation or drying of the skin.
Eyes	:	Dust contact with the eyes can lead to mechanical irritation.
Inhalation	:	May cause nose, throat, and lung irritation.

Carcinogenicity

Material	IARC	NTP	OSHA
Titanium dioxide	2B		

SECTION 3. COMPOSITION/INFORMATION ON INGREDIENTS

Material Safety Data Sheet

DuPont™ Ti-Pure® Titanium Dioxide Pigment - Plastics Grades

Version 4.1

Revision Date 11/05/2012 Ref. 150000002100

This SDS adheres to the standards and regulatory requirements of the United States and may not meet the regulatory requirements in other countries.

SECTION 1. PRODUCT AND COMPANY IDENTIFICATION

Product name : DuPont™ Ti-Pure® Titanium Dioxide Pigment - Plastics Grades
Product Grade/Type : R-101, R-102, R-103, R-104, R-105, R-108, R-350

MSDS Number : 150000002100

Product Use : Colouring agents, pigments

Manufacturer : DuPont
1007 Market Street
Wilmington, DE 19898

Product Information : 1-302-774-1000
Medical Emergency : 1-800-441-3637 (outside the U.S. 1-302-774-1139)
Transport Emergency : CHEMTREC: 1-800-424-9300 (outside the U.S. 1-703-527-3887)

SECTION 2. HAZARDS IDENTIFICATION

Potential Health Effects

Skin : Contact with dust can cause mechanical irritation or drying of the skin.

Eyes : Dust contact with the eyes can lead to mechanical irritation.

Inhalation : May cause nose, throat, and lung irritation.

Carcinogenicity

Material	IARC	NTP	OSHA
Titanium dioxide	2B		

SECTION 3. COMPOSITION/INFORMATION ON INGREDIENTS

Component	CAS-No.	Concentration
Titanium dioxide	13463-67-7	90 - 99 %
Aluminum hydroxide	21645-51-2	0 - 5 %
Silicon dioxide, amorphous	7631-86-9	0 - 4 %

SECTION 4. FIRST AID MEASURES

Skin contact	:	Wash off with soap and water.
Eye contact	:	Rinse with plenty of water.
Inhalation	:	Remove person to fresh air. If signs/symptoms continue, get medical attention.
Ingestion	:	No specific intervention is indicated. Consult a physician if necessary.

SECTION 5. FIREFIGHTING MEASURES

Flammable Properties		
Flash point	:	does not flash
Suitable extinguishing media	:	Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.
Firefighting Instructions	:	The product itself does not burn.

SECTION 6. ACCIDENTAL RELEASE MEASURES

NOTE: Review FIRE FIGHTING MEASURES and HANDLING (PERSONNEL) sections before proceeding with clean-up. Use appropriate PERSONAL PROTECTIVE EQUIPMENT during clean-up.

Safeguards (Personnel) : Avoid breathing dust.

Spill Cleanup : Pick up and arrange disposal without creating dust. After cleaning, flush away traces with water.

Accidental Release Measures : Do not flush into surface water or sanitary sewer system.

SECTION 7. HANDLING AND STORAGE

Handling (Personnel) : Avoid breathing dust.
In the manufacture of titanium dioxide, product is packaged at temperatures of approximately 100 to 120 C (212 to 248 F). When pigment is shipped shortly after manufacture, it may stay hot for a very long time depending on ambient temperatures and inventory storage practices. Use caution while handling hot pigment to prevent burns to personnel. Use caution in solvent applications to prevent ignition of solvent.
Wash hands before breaks and at the end of workday.

Handling (Physical Aspects) : An electrostatic charge can potentially build up when pouring or conveying product from plastic bags. Do not use plastic bags in the presence of flammable or explosive vapors.
This is a fully oxidized mineral product. As such it cannot support combustion or participate in a dust explosion.

Storage : Keep container tightly closed in a dry and well-ventilated place.

SECTION 8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls : Use sufficient ventilation to keep employee exposure below recommended limits.

Personal protective equipment

Respiratory protection	: When workers are facing concentrations above the exposure limit they must use appropriate certified respirators.
Hand protection	: Additional protection: Gloves
Eye protection	: Safety glasses with side-shields

Exposure Guidelines
Exposure Limit Values

Titanium dioxide

PEL:	(OSHA)	15 mg/m3	8 hr. TWA	Total dust.
TLV	(ACGIH)	10 mg/m3	TWA	
AEL *	(DUPONT)	10 mg/m3	8 & 12 hr. TWA	Total dust.
AEL *	(DUPONT)	5 mg/m3	8 & 12 hr. TWA	Respirable dust.

* AEL is DuPont's Acceptable Exposure Limit. Where governmentally imposed occupational exposure limits which are lower than the AEL are in effect, such limits shall take precedence.

SECTION 9. PHYSICAL AND CHEMICAL PROPERTIES

Form	: crystalline
Color	: white
Odor	: odourless
pH	: not applicable
% Volatile	: 0 %
Specific gravity	: 3.6 - 4.3
Water solubility	: insoluble

SECTION 10. STABILITY AND REACTIVITY

Stability	: Stable
Incompatibility	: None.

SECTION 11. TOXICOLOGICAL INFORMATION

DuPont™ Ti-Pure® Titanium Dioxide Pigment - Plastics Grades

Inhalation 4 h LC50	: > 6.82 mg/l , rat
Oral LD50	: > 5,000 mg/kg , rat
Skin irritation	: Slight or no skin irritation, rabbit
Eye irritation	: Slight or no eye irritation, rabbit
Sensitisation	: Did not cause sensitization on laboratory animals., mouse Did not cause sensitization on laboratory animals., guinea pig
Repeated dose toxicity	: Oral rat No toxicologically significant effects were found. Inhalation rat No toxicologically significant effects were found.
Carcinogenicity	: In lifetime inhalation studies rats were exposed for 2 years to respectively 10, 50 and 250 mg/m3 of respirable TiO2. Slight lung fibrosis was observed at 50 and 250 mg/m3 levels. Microscopic lung tumours were also observed in 13 percent of the rats exposed to 250 mg/m3, an exposure level that caused lung overloading and impairment of rat lungs clearance mechanisms. In further studies, these tumours were found to occur only under particle overload conditions in a uniquely sensitive species, the rat,

and have little or no relevance for humans. The pulmonary inflammatory response to TiO2 particles exposure was also found to be much more severe in rats than in other rodent species.

In February 2006, IARC has re-evaluated Titanium dioxide as pertaining to Group 2B: "possibly carcinogenic to humans", based upon inadequate evidence in humans and sufficient evidence in experimental animals for the carcinogenicity of titanium dioxide. IARC evaluation guidelines consider the generation of tumours, in 2 different studies within the same animal species, to be adequate criteria for an assessment of sufficient evidence.

The conclusions of several epidemiology studies on more than 20000 TiO2 industry workers in Europe and the USA did not suggest a carcinogenic effect of TiO2 dust on the human lung. Mortality from other chronic diseases, including other respiratory diseases, was also not associated with exposure to TiO2 dust.

Based upon all available study results, DuPont scientists conclude that titanium dioxide will not cause lung cancer or chronic respiratory diseases in humans at concentrations experienced in the workplace.

Mutagenicity : Did not cause genetic damage in animals.
Tests on bacterial or mammalian cell cultures did not show mutagenic effects.

SECTION 12. ECOLOGICAL INFORMATION

Aquatic Toxicity

DuPont™ Ti-Pure® Titanium Dioxide Pigment - Plastics Grades

96 h LC50 : Pimephales promelas (fathead minnow) > 1,000 mg/l

72 h EC50 : Pseudokirchneriella subcapitata (green algae) 61 mg/l

48 h EC50 : Daphnia magna (Water flea) > 1,000 mg/l

SECTION 13. DISPOSAL CONSIDERATIONS

Waste Disposal : Dispose of in accordance with local regulations.

SECTION 14. TRANSPORT INFORMATION

Not regulated in transportation by DOT/IMO/IATA.

SECTION 15. REGULATORY INFORMATION

EINECS Status	:	On the inventory, or in compliance with the inventory
TSCA Status	:	On the inventory, or in compliance with the inventory
AICS Status	:	On the inventory, or in compliance with the inventory
DSL Status	:	On the inventory, or in compliance with the inventory
ENCS (JP) Status	:	On the inventory, or in compliance with the inventory
KECI (KR) Status	:	On the inventory, or in compliance with the inventory
PICCS (PH) Status	:	On the inventory, or in compliance with the inventory
INV (CN) Status	:	On the inventory, or in compliance with the inventory
NZ HSNO Status	:	Exempt
SARA 313 Regulated Chemical(s)	:	SARA 313: This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.
California Prop. 65	:	WARNING! This product contains a chemical known to the State of California to cause cancer.The listing of titanium dioxide is for "airborne, unbound particles of respirable size." The listing is not applicable to titanium dioxide when it remains bound within a product matrix.
PA Right to Know Regulated Chemical(s)	:	Substances on the Pennsylvania Hazardous Substances List present at a concentration of 1% or more (0.01% for Special Hazardous Substances): Titanium dioxide , Silicon dioxide, amorphous

NJ Right to Know Regulated Chemical(s)	:	Substances on the New Jersey Workplace Hazardous Substance List present at a concentration of 1% or more (0.1% for substances identified as carcinogens, mutagens or teratogens): Titanium dioxide , Silicon dioxide, amorphous

SECTION 16. OTHER INFORMATION

		HMIS
Health	:	1
Flammability	:	0
Reactivity/Physical hazard	:	0
PPE	:	Personal Protection rating to be supplied by user depending on use conditions.

Restrictions for use : Ti-Pure® products may not be directly added to food or pharmaceuticals and are not recommended for use in medical devices or cosmetics.

Do not use DuPont materials in medical applications involving implantation in the human body or contact with internal body fluids or tissues unless the material has been provided from DuPont under a written contract that is consistent with DuPont policy regarding medical applications and expressly acknowledges the contemplated use. For further information, please contact your DuPont representative. You may also request a copy of the DuPont POLICY Regarding Medical Applications H-50103-3 and DuPont CAUTION Regarding Medical Applications H-50102-3.

Ti-Pure® is a Registered Trademark of E. I. du Pont de Nemours and Company.

For specific information on composition and properties, see DuPont™ Ti-Pure® Titanium Dioxide Pigment literature. Please see www2.dupont.com/Titanium_Technologies/en_US/ for the latest version of this MSDS.

Contact person : MSDS Coordinator DuPont Titanium Technologies; Wilmington, DE 19898; Telephone (800) 441-9485

The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text.

Significant change from previous version is denoted with a double bar.

APPENDIX 6-5

MDEQ PERMIT CORROSION MONITORING RESULTS 2016-2017

MDEQ Permit MSI1001 Well 2 Corrosion Monitoring Results

Coupon No.	**Date Installed**	**Date Removed**	**AlloyDesign**	**Alloy Name**	Corrosion Rate (mpy)	Description of Corrosion Attack
2A	10/15/2013	1/13/2014	R50400	TI2	0.0015	1 - Unattacked
2A	10/15/2013	1/13/2014	R52400	TIPD	0.0030	1 - Unattacked
2B	1/13/2014	4/22/2014	R50400	Titanium Grade 2 (TI2)	0.0017	1 - Unattacked, 3 - Superficial corrosion
2B	1/13/2014	4/22/2014	R52400	Titanium Grade 7 (TIPD)	0.0017	1 - Unattacked
2A	4/22/2014	7/14/2014	R50400	TI2	0.0083	1 - Unattacked
2A	4/22/2014	7/14/2014	R52400	TIPD	0.0049	1 - Unattacked
Well Stopped Injecting on 7/14/14 for Workover						
Well Workover 7/29/14 to 10/15/14						
2B	10/16/2014	1/13/2015	R50400	Titanium Grade 2 (TI2)	0.0000	1 - Unattacked
2B	10/16/2014	1/13/2015	R52400	Titanium Grade 7 (TIPD)	0.0000	1 - Unattacked
2A	1/13/2015	4/9/2015	R50400	TI2	0.0016	superficial

Coupon No.	**Date Installed**	**Date Removed**	**AlloyDesign**	**Alloy Name**	Corrosion Rate (mpy)	Description of Corrosion Attack
2A	1/13/2015	4/9/2015	R52400	TIPD	0.0065	superficial
2B	4/9/2015	7/15/2015	R50400	Titanium Grade 2 (TI2)	0.0016	Unattacked, Superficial corrosion. HAS MECHANICAL SCUFF ON FACE OF COUPON
2B	4/9/2015	7/15/2015	R52400	Titanium Grade 7 (TIPD)	0.0065	Unattacked, Superficial corrosion
2A	7/15/2015	10/9/2015	R50400	TI2	0.0016	superficial
2A	7/15/2015	10/9/2015	R52400	TIPD	0.0016	superficial
2B	10/9/2015	1/13/2016	R50400	Titanium Grade 2 (TI2)	0.0029	superficial
2B	10/9/2015	1/13/2016	R52400	Titanium Grade 7 (TIPD)	0.0233	superficial
2A	1/13/2016	4/19/2016	R50400	TI2	0.0057	superficial
2A	1/13/2016	4/19/2016	R52400	TIPD	0.0058	superficial
2B	4/19/2016	7/13/2016	R50400	Titanium Grade 2 (TI2)	0.0000	superficial
2B	4/19/2016	7/13/2016	R52400	Titanium Grade 7 (TIPD)	-0.0033	superficial

Coupon No.	**Date Installed**	**Date Removed**	**AlloyDesign**	**Alloy Name**	Corrosion Rate (mpy)	Description of Corrosion Attack
2A	7/13/2016	10/18/2016	R50400	TI2	0.0000	superficial
2A	7/13/2016	10/18/2016	R52400	TIPD	0.0000	superficial
2B	10/18/2016	4/13/2017	R50400	Titanium Grade 2 (TI2)	0.0045	superficial
2B	10/18/2016	4/13/2017	R52400	Titanium Grade 7 (TIPD)	0.0122	superficial
2A	1/18/2017	4/13/2017	R50400	TI2	0.0049	superficial
2A	1/18/2017	4/13/2017	R52400	TIPD	0.0099	superficial

MDEQ Permit MSI1001 Well 3 Corrosion Monitoring Results

Coupon No.	Date Installed	Date Removed	AlloyDesign	Alloy Name	Corrosion Rate (mpy)	Description of Corrosion Attack
3A	12/3/2013	3/18/2014	R50400	TI2	0.0000	1 - Unattacked
3A	12/3/2013	3/18/2014	R52400	TI7	0.0000	1 - Unattacked
3B	3/18/2014	6/11/2014	R50400	TI2	0.1000	1 - Unattacked
3B	3/18/2014	6/11/2014	R52400	TI7	0.0100	1 - Unattacked; Calculated Density is not within 5% of UNS Density
3A	6/11/2014	9/23/2014	R50400	TI2	0.0000	1 - Unattacked
3A	6/11/2014	9/23/2014	R52400	TI7	0.0000	1 - Unattacked
3B	9/23/2014	12/16/2014	R50400	TI2	0.0100	1 - Unattacked
3B	9/24/2014	12/16/2014	R52400	TI7	0.0100	1 - Unattacked
3A	12/16/2014	3/18/2015	R50400	TI2	-0.0030	Superficial
3A	12/16/2014	3/18/2015	R52400	TI7	0.0075	Superficial

Coupon No.	Date Installed	Date Removed	AlloyDesign	Alloy Name	Corrosion Rate (mpy)	Description of Corrosion Attack
3B	3/18/2015	6/10/2015	R50400	TI2	0.0049	Unattacked, Superficial corrosion
3B	3/18/2015	6/10/2015	R52400	TI7	0.0050	Unattacked, Superficial corrosion
3A	6/10/2015	9/24/2015	R50400	TI2	0.0013	superficial
3A	6/10/2015	9/24/2015	R52400	TI7	0.0039	superficial
3B	9/24/2015	12/21/2015	R50400	Titanium Grade 2 (TI2)	0.0016	superficial
3B	9/24/2015	12/21/2015	R52400	Titanium Grade 7 (TI7)	0.0078	superficial
3A	12/21/2015	3/22/2016	R50400	TI2	0.0030	superficial
3A	12/21/2015	3/22/2016	R52400	TI7	0.0045	superficial
3B	3/22/2016	6/7/2016	R50400	Titanium Grade 2 (TI2)	0.0162	superficial
3B	3/22/2016	6/7/2016	R52400	Titanium Grade 7 (TI7)	0.0072	superficial
3A	6/7/2016	9/20/2016	R50400	TI2	0.0090	superficial

Coupon No.	**Date Installed**	**Date Removed**	**AlloyDesign**	**Alloy Name**	Corrosion Rate (mpy)	Description of Corrosion Attack
3A	6/7/2016	9/20/2016	R52400	TI7	0.0091	superficial
3B	9/20/2016	12/20/2016	R50400	Titanium Grade 2 (TI2)	0.0167	superficial
3B	9/20/2016	12/20/2016	R52400	Titanium Grade 7 (TI7)	0.0153	superficial
3A	12/20/2016	3/21/2017	R50400	TI2	0.0000	superficial
3A	12/20/2016	3/21/2017	R52400	TI7	0.0082	superficial
3B	3/21/2017	6/7/2017	R50400	Titanium Grade 2 (TI2)	0.0000	superficial
3B	3/21/2017	6/7/2017	R52400	Titanium Grade 7 (TI7)	0.0000	superficial

MDEQ Permit MSI1001 Well 4 Corrosion Monitoring Results

Coupon No.	**Date Installed**	**Date Removed**	**AlloyDesign**	**Alloy Name**	Corrosion Rate (mpy)	Description of Corrosion Attack
4B	11/15/2013	2/10/2014	R50400	TI2	-0.0034	3 - Superficial Corrosion
4B	11/15/2013	2/10/2014	R52400	TI7	-0.0066	3 - Superficial Corrosion
4A	2/10/2014	5/13/2014	R50400	TI2	0.0000	1 - Unattacked
4A	2/10/2014	5/13/2014	R52400	Titanium Grade 7 (TIPD)	0.0100	3 - Superficial corrosion
4B	5/13/2014	8/13/2014	R50400	TI2	0.0000	1 - Unattacked
4B	5/13/2014	8/13/2014	R52400	TI7	0.0000	1 - Unattacked
4A	8/13/2014	11/13/2014	R50400	TI2	0.0000	1 - Unattacked
4A	8/13/2014	11/13/2014	R52400	Titanium Grade 7 (TIPD)	0.0000	1 - Unattacked
4B	11/13/2014	2/3/2015	R50400	TI2	-0.0034	Superficial
4B	11/13/2014	2/3/2015	R52400	TI7	-0.0066	Superficial

Coupon No.	**Date Installed**	**Date Removed**	**AlloyDesign**	**Alloy Name**	Corrosion Rate (mpy)	Description of Corrosion Attack
4A	2/3/2015	5/4/2015	R50400	TI2	0.0000	Superficial
4A	2/3/2015	5/4/2015	R52400	Titanium Grade 7 (TIPD)	0.0000	Superficial
4B	5/4/2015	8/20/2015	R50400	TI2	0.0000	Little to no attack/superficial
4B	5/4/2015	8/20/2015	R52400	TI7	-0.0013	Little to no attack/superficial
4A	8/20/2015	11/11/2015	R50400	TI2	0.0000	Little to no attack/superficial
4A	8/20/2015	11/11/2015	R52400	TIPD	0.0000	Little to no attack/superficial
4B	11/11/2015	2/16/2016	R50400	TI2	0.0088	Little to no attack/superficial
4B	11/11/2015	2/16/2016	R52400	TI7	0.0086	Little to no attack/superficial
4A	2/16/2016	4/17/2016	R50400	TI2	0.0068	Little to no attack/superficial
4A	2/16/2016	4/17/2016	R52400	TIPD	0.0022	Little to no attack/superficial
4B	4/17/2016	8/24/2016	R50400	TI2	0.0000	Little to no attack/superficial

Coupon No.	Date Installed	Date Removed	AlloyDesign	Alloy Name	Corrosion Rate (mpy)	Description of Corrosion Attack
4B	4/17/2016	8/24/2016	R52400	TI7	0.0031	Little to no attack/superficial
4A	8/24/2016	11/15/2016	R50400	TI2	0.0000	Little to no attack/superficial
4A	8/24/2016	11/15/2016	R52400	TIPD	0.0000	Little to no attack/superficial
4B	11/15/2016	2/23/2017	R50400	TI2	0.0000	Little to no attack/superficial
4B	11/15/2016	2/23/2017	R52400	TI7	0.0000	Little to no attack/superficial
4A	2/23/2017	5/9/2017	R50400	TI2	0.0037	Little to no attack/superficial
4A	2/23/2017	5/9/2017	R52400	TIPD	0.0090	Little to no attack/superficial

MDEQ Permit MSI1001 Well 5 Corrosion Monitoring Results

Coupon No.	Date Installed	Date Removed	AlloyDesign	Alloy Name	Corrosion Rate (mpy)	Description of Corrosion Attack
5A	12/16/2013	3/3/2014	R50400	TI2	0.0000	1 - Unattacked
5A	12/16/2013	3/3/2014	R52400	TI7	0.0000	1 - Unattacked
5B	3/3/2014	6/24/2014	R50400	TI12	0.0000	1 - Unattacked
5B	3/3/2014	6/24/2014	R52400	TI17	0.0000	1 - Unattacked
5A	6/24/2014	9/3/2014	R50400	TI2	0.0000	1 - Unattacked
5A	6/24/2014	9/3/2014	R52400	TI7	0.0000	1 - Unattacked
5B	9/3/2014	12/2/2014	R50400	TI12	0.0000	1 - Unattacked
5B	9/3/2014	12/2/2014	R52400	TI17	0.0000	1 - Unattacked
5A	12/2/2014	3/4/2015	R50400	TI2	0.0000	1 - Unattacked
5A	12/2/2014	3/4/2015	R52400	TI7	0.0000	1 - Unattacked

Coupon No.	Date Installed	Date Removed	AlloyDesign	Alloy Name	Corrosion Rate (mpy)	Description of Corrosion Attack
5B	3/4/2015	4/3/2015	R50400	TI2	-0.0876	Unattacked - Superficial Corrosion
5B	3/4/2015	4/3/2015	R52400	TI7	-0.0503	Unattacked - Superficial Corrosion
5A	4/3/2015	4/21/2015	R50400	TI2	See at right	"very low to now corrosion and superficial in nature."
5A	4/3/2015	4/21/2015	R52400	TI7	See at right	"very low to now corrosion and superficial in nature."
Well Workover 4/22/2015 to 9/13/2015						
5B	9/15/2015	12/9/2015	R50400	TI2	0.0000	Superficial
5B	9/15/2015	12/9/2015	R52400	TI7	0.0016	Superficial
5A	12/9/2015	3/9/2016	R50400	TI2	-0.0152	Superficial
5A	12/9/2015	3/9/2016	R52400	TI7	-0.0030	Superficial
5B	3/9/2016	6/21/2016	R50400	TI2	-0.0026	Superficial
5B	3/9/2016	6/21/2016	R52400	TI7	0.0013	Superficial
5A	6/21/2016	9/16/2016	R50400	TI2	0.0000	Superficial

Coupon No.	**Date Installed**	**Date Removed**	**AlloyDesign**	**Alloy Name**	Corrosion Rate (mpy)	Description of Corrosion Attack
5A	6/21/2016	9/16/2016	R52400	TI7	0.0000	Superficial
5B	9/16/2016	12/6/2016	R50400	TI2	0.0065	Superficial
5B	9/16/2016	12/6/2016	R52400	TI7	0.0033	Superficial
5A	12/6/2016	3/2/2017	R50400	TI2	0.0016	Superficial
5A	12/6/2016	3/2/2017	R52400	TI7	0.0080	Superficial
5B	3/2/2017	6/15/2017	R50400	TI2	0.0013	Superficial
5B	3/2/2017	6/15/2017	R52400	TI7	0.0000	Superficial